PB80-197072

Control Assay Development: Methodology and Laboratory Verification

Catalytic, Inc.
Philadelphia, PA

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

Jan 80

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-80-002	2.	3. RECIPIENT'S ACCESSION NO. PB 80 197072
4. TITLE AND SUBTITLE Control Assay Development: Methodology and Laboratory Verification		5. REPORT DATE January 1980
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) W. F. Longaker, S. M. Hossain, and A. B. Cherry		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Catalytic, Inc. 1500 Market Street Philadelphia, Pennsylvania 19102		10. PROGRAM ELEMENT NO. EHE623A
		11. CONTRACT/GRANT NO. 68-02-2167, Tasks 9 and 12
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Task Final; 7/78 - 7/79
		14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Robert A. McAllister, Mail Drop 61, 919/541-2160.

16. ABSTRACT

The report describes Control Assay Development (CAD), a data acquisition program designed to evaluate the potential applicability of various treatment processes for the control of solid, liquid, and gaseous emissions from coal conversion plants. The CAD program described could be used to provide data for evaluating selected treatment technologies for coal conversion wastewaters. Detailed descriptions of all CAD screening procedures and equipment required for outfitting a mobile laboratory are presented. Laboratory tests were conducted to assess the adequacy of the proposed designs and operating procedures, and to verify the use of a dry bacterial culture for biological oxidation studies. A number of design modifications were recommended, based on the laboratory tests. Insufficient benefit is derived from the use of a dry bacterial culture during the bio-oxidation screening procedure to warrant its adoption in the testing procedure.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Oxidation	Pollution Control	13B	07B,07C
Assaying		Stationary Sources	14B	
Coal		Control Assay Development	08G,21D	
Coal Gasification			13H	
Waste Water		Biological Oxidation		
Biology		Coal Conversion	06C	

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

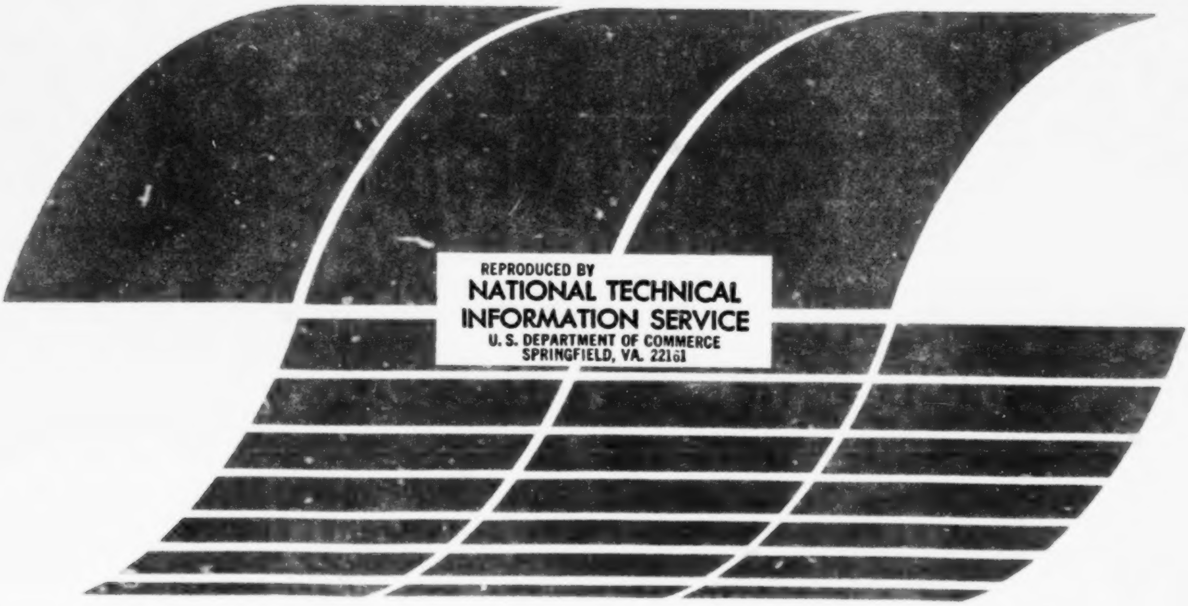
EPA-600/7-80-002
January 1980

PB80-157072

EPA

Control Assay Development: Methodology and Laboratory Verification

Interagency Energy/Environment R&D Program Report



REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the INTERAGENCY ENERGY-ENVIRONMENT RESEARCH AND DEVELOPMENT series. Reports in this series result from the effort funded under the 17-agency Federal Energy/Environment Research and Development Program. These studies relate to EPA's mission to protect the public health and welfare from adverse effects of pollutants associated with energy systems. The goal of the Program is to assure the rapid development of domestic energy supplies in an environmentally-compatible manner by providing the necessary environmental data and control technology. Investigations include analyses of the transport of energy-related pollutants and their health and ecological effects; assessments of, and development of, control technologies for energy systems; and integrated assessments of a wide range of energy-related environmental issues.

EPA REVIEW NOTICE

This report has been reviewed by the participating Federal Agencies, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Government, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/7-80-002
January 1980

Control Assay Development:
Methodology and Laboratory Verification

by

W.F. Longaker, S.M. Hossain, and A.B. Cherry

Catalytic, Inc.
1500 Market Street
Philadelphia, Pennsylvania 19102

Contract No. 68-02-2167
Task No. 9 and 12
Program Element No. EHE623A

EPA Project Officer: Robert A. McAllister

Industrial Environmental Research Laboratory
Office of Environmental Engineering and Technology
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

iB

ACKNOWLEDGEMENTS

The following personnel of Catalytic, Inc. made major contributions to the technical work performed under this directive:

A. B. Cherry
S. M. Hossain
W. F. Longaker
J. W. Mitchell
J. C. Watt

Special acknowledgement is made to R. P. Hangebrauck, initiator of the concept of Control Assay Development as an approach for gathering basic environmental data, and also to T. K. Janes, W. J. Rhodes and C. A. Vogel of the U. S. Environmental Protection Agency for their continuing advice, counsel and guidance throughout the project.

CONTENTS

Page

ACKNOWLEDGEMENTS i
ABSTRACT ii
FIGURES vi
TABLES vii

SECTION 1 CONTROL ASSAY DEVELOPMENT 1
- 1.1 Introduction 1
- 1.2 Application 2
- 1.3 Implementation 3

SECTION 2 WASTEWATER METHODOLOGY 5
- 2.1 Background 5
  - 2.1.1 Sampling Procedures 15
  - 2.1.2 Sample Analysis 15
- 2.2 Pretreatment 17
  - 2.2.1 General Comments 17
  - 2.2.2 Phenol Removal 18
  - 2.2.3 Hydrogen Sulfide and Ammonia Removal 19
  - 2.2.4 Cyanide Removal 22
- 2.3 Preparation of Composite Sample 23
- 2.4 Screening Procedures 25
  - 2.4.1 Solids Removal 25
  - 2.4.2 Carbon Adsorption 27
  - 2.4.3 Biological Oxidation 36
  - 2.4.4 Ion Exchange 43
  - 2.4.5 Chemical Oxidation 46

SECTION 3 GASEOUS EMISSION METHODOLOGY 48
- 3.1 Background 48
  - 3.1.1 Module Description 49
  - 3.1.2 Applicability 51
  - 3.1.3 Sampling 52
  - 3.1.4 Analysis 54
- 3.2 Preliminary Measurements 55
  - 3.2.1 Introduction 55
  - 3.2.2 Apparatus 56
  - 3.2.3 Reagents 56
  - 3.2.4 Stack Geometry, Temperature and Gas Velocity Measurements 56
  - 3.2.5 Moisture Content 56
  - 3.2.6 Gas Composition 57

CONTENTS (Continued)

Page

3.3 Screening Procedures with Carbon 58
3.3.1 Introduction 58
3.3.2 Summary of Method 59
3.3.3 Apparatus 59
3.3.4 Reagents 59
3.3.5 Preparation 59
3.3.6 Sampling Procedures 63
3.3.7 Sample Handling Procedures 64
3.4 Gas Screening Procedures with Scrubbing Module 65
3.4.1 Introduction 65
3.4.2 Summary of Method 65
3.4.3 Apparatus 66
3.4.4 Reagents 66
3.4.5 Preparation 66
3.4.6 Sampling Procedure 69
3.4.7 Sample Handling Procedures 70
3.5 Gas Screening Procedures with Scrubbing and Carbon Adsorption Modules 71
3.5.1 Introduction 71
3.5.2 Summary of Method 71
3.5.3 Apparatus 71
3.5.4 Reagents 71
3.5.5 Preparation 71
3.5.6 Sampling Procedures 73
3.5.7 Sample Handling Procedures 74

SECTION 4 SOLIDS METHODOLOGY 75
4.1 Background 75
4.2 Screening Procedures 77
4.2.1 Applicability 77
4.2.2 Current Testing 77
4.2.3 Supplemental Testing 78

SECTION 5 LABORATORY VERIFICATION 79

SECTION 6 WASTEWATER SCREENING 82
6.1 Synthetic Wastewater Composition 82
6.2 Solids Separation 85
6.2.1 Initial Concepts 85
6.2.2 Selected Alternative 86
6.2.3 Test Work 86
6.2.4 Discussion of Results 86
6.3 Carbon Adsorption 87
6.3.1 Initial Concepts 87
6.3.2 Selected Alternative 89
6.3.3 Test Work 89
6.2.4 Discussion of Results 91

CONTENTS (Continued)

Page

6.4 Biological Oxidation 92
6.4.1 Initial Concepts 92
6.4.2 Selected Alternative 93
6.4.3 Test Work 93
6.4.3.1 Batch Testing 97
6.4.3.2 Continuous Units 99
6.4.3.3 Control Assay Batch Test 99
6.4.4 Discussion of Results 108
6.5 Ion Exchange 111
6.5.1 Initial Concepts 111
6.5.2 Selected Alternative 111
6.5.3 Test Work 111
6.5.4 Discussion of Results 112

SECTION 7 CONCLUSIONS AND RECOMMENDATIONS - WASTEWATER 114

SECTION 8 GASEOUS EMISSIONS SCREENING 117
8.1 Gas Blend Composition 117
8.2 Modified Sampling System Evaluation 117
8.2.1 Initial Concepts 117
8.2.2 Selected Alternative 120
8.2.3 Test Work 120
8.2.4 Discussion of Results 124

SECTION 9 CONCLUSIONS AND RECOMMENDATIONS - GASEOUS EMISSIONS 130

REFERENCES 131

FIGURES

Number Page

1. Wastewater test sequence 6
2. Phenol extraction apparatus 20
3. Typical adsorption isotherm 32
4. Carbon column apparatus 34
5. Gaseous emission screening sequence 47
6. Gaseous emission screening train alternatives 53
7. Grab sampling bulb 60
8. Carbon screening train 61
9. Grab sampling bulb with dual stopcock arrangement 62
10. Detail of scrubber 67
11. Scrubber screening train 68
12. Combination scrubbing and carbon adsorption screening train 72
13. Initial wastewater test sequence 80
14. Carbon isotherm plot 90
15. COD and BOD addition by dry bacteria 98
16. Continuous biological reactor results 107
17. Results for synthetic waste sample 115
18. Scrubber evaluation apparatus 118
19. Gaseous emission test sequence 119
20. Combination scrubbing and carbon adsorption screening train.............................. 121

TABLES

Number Page

1. Coal Gasification Wastewater Sources and Characteristics... 8
2. Coal Liquefaction Plant Wastewater Sources and Characteristics.. 9
3. Treatment Technologies Available for Specified Pollutants.. 10
4. Data Sheet for Composite Sample 24
5. Activated Sludge Seed Acclimation Schedule 40
6. Organic Composition of Synthetic Waste 83
7. Inorganic Components of Synthetic Waste 84
8. Activated Carbon Test Results 88
9A. Air Stripping/Oxidation Tests 95
9B. Effect of Volume on Air Stripping/Oxidation 95
10. Dry Bacteria - COD and BOD Data 96
11. Biological Oxidation - Batch Reactor Results 100
12. Continuous Biosystem Treatability Data - Unit A 101
13. Continuous Biosystem Treatability Data - Unit B 104
14. Results of Ion Exchange Testing 113
15. Screening Train Pressure Drop Testing 123
16. Run #1 - Scrubber Evaluation 125
17. Run #2 - Scrubber Evaluation 126
18. Run #1 - Carbon Adsorption 127
19. Run #1 - Scrubbing Followed by Carbon Adsorption 128

SECTION 1

CONTROL ASSAY DEVELOPMENT

1.1 INTRODUCTION

Control Assay Development (CAD) is a program designed to provide information for preliminary evaluation of the effectiveness of selected control techniques for removing pollutants from multimedia discharges. CAD is a significant and important aspect of the EPA's data acquisition program for environmental assessment of fuel conversion/utilization systems.

All coal conversion and associated products/byproducts upgrading processes generate gaseous, liquid and solid wastes. Some of the more important control needs include H_2S, COS, mercaptans, SO_2, NO_x, hydrocarbons and particulate removal from gaseous emissions; removal of phenol, ammonia, sulfide, organics, heavy metals and cyanides from aqueous waste streams; and prevention of solid waste leachate problems. When such pollutants are removed from waste streams and converted to useable products, downstream waste treatment problems and environmental impacts are automatically improved.

More data are needed on the detailed characteristics of the various products, byproducts and waste streams generated by coal conversion systems. Limited upgrading tests have been conducted with coal conversion products and byproducts. More tests are necessary to characterize effluent streams, product/byproduct quality and determine catalyst life. Results from these tests and sampling and analysis campaigns will undoubtedly show the need for additional control technology development and are, therefore, an important part of the overall environmental management program.

1.2 APPLICATION

Relatively little operating data on control technology for laboratory, pilot or commercial-scale coal conversion systems exist in the literature. Data acquisition by actual field testing should be given high priority. Laboratory scale tests that can be performed in the field for control technology assessment of treatment operations/processes are discussed in this report.

The CAD approach will be quite useful under circumstances where control technology has not been defined, or where environmentally satisfactory interim methods are being used which may not represent best technology/economic practice on a commercial scale. Pilot plants and development units for new coal conversion technologies are examples of these situations. In such cases, CAD byproduct removal operations may be employed usually on a temporary basis to remove pollutants which would not normally be discharged from a full-scale commercial facility, thereby rendering the test waste samples more typical of the discharges that will eventually be generated.

In conceiving CAD methodologies, a basic assumption is made that the program would operate in conjunction with an IERL Level 1 sampling and analysis (S/A) effort. The CAD team will be responsible for producing treated samples which will be turned over to the IERL Level 1 S/A team for analyses. CAD procedures also include special field analyses that aid in the selection of appropriate control assay operations. Any analyses which are required for proper operation of a CAD treatment process such as pH, oxygen uptake rate, etc., will be performed by members of the CAD field team. Level 1 chemical and bioassay procedures will be used to provide test data for evaluating the effectiveness of the treatment schemes employed.

For every raw sample processed under CAD procedures, a number of treated effluent samples will be produced. Therefore, judgement should be applied in selecting raw samples. If it is known from previous experience that some of the effluents may not be harmful, or that their treatment schemes and ultimate fate are well established, then they should not be included in the CAD program. For example, raw water treatment system effluents are well characterized and their disposal options well known. Therefore, these would not normally be included in the CAD schedules, even though they might be included in the Level 1 S/A effort.

1.3 IMPLEMENTATION

Before the actual CAD effort is initiated, data needs must be established and used to help identify test requirements as well as any anticipated problems. These requirements are similar to those identified under the IERL Level 1 S/A Schemes.

1. Process data such as temperature and pressure must be known.
2. A pre-test site survey must be made to verify process data and tentative sample points selected.
3. Pre-test site preparation must be specified to have sample points accessible and outfitted with appropriate nozzles, valves, etc. Electrical, water and other services must be provided, where needed.

Detailed process data are necessary for the CAD effort for the following reasons:

1. From a knowledge of the process and the composition of the input materials and products, preliminary estimates about pollutants likely to be found in waste streams are made. This analysis will be helpful in the planning of control assay operations.
2. Prior knowledge of the waste stream flow rates, their pressures and temperatures must be known for selection of proper sampling methodology and also for preparing composite waste samples from various individual streams.
3. Familiarization with the process and the plant will ensure knowledge of where to look for waste streams.

The raw samples and the treated effluent samples will be analyzed by the Level 1 S/A protocols. Some of these analyses will be performed in the field and some in the home laboratory. In certain instances, additional tests are recommended to aid CAD evaluations.

A phased approach is recommended for data gathering. The first phase, CAD-1, will utilize control assay operations selected from classical and more common treatment operations/processes. CAD-1 concepts and procedures, the subject matter of this report, are essentially screening studies designed to gather basic, broad-based indicative information where little or none currently exist. The second phase effort (with the benefit of CAD-1 and Level 1 sampling and analysis results) will concentrate on those streams previously found by CAD-1 to be exceeding the effluent decision criteria limitations. These problem streams will be re-examined using additional control assay operations more specifically designed to remove particular problem pollutants.

The procedure to gather raw samples for the CAD Phase 1 and 2 efforts will be essentially the same as for Level 1 and Level 2 S/A techniques. However, sample sources and quantities needed for CAD will differ from those specified by S/A procedures.

CAD wastewater screening tests include the following pretreatment operations: solvent extraction of phenol, ammonia and hydrogen sulfide stripping, and chemical oxidation for cyanides. Pretreated wastewater will then be processed through the following operations: filtration, bio-oxidation, activated carbon adsorption and ion exchange.

CAD procedures for gaseous emissions will include unit operations for the removal of particulates and gases/vapors. Particulate will be removed through a cyclone/filter assembly. Gases and vapors will be removed through the following operations: gas cooling (indirect water cooling); alkaline scrubbing; and activated carbon adsorption.

The principal control approaches for solids (e.g., resource recovery, incineration and fixation) are not easily conducted in the field. Incineration equipment becomes impractical to outfit and operate in a CAD mobile facility. Chemical fixation or encapsulation techniques commercially are proprietary and samples would have to be forwarded to a selected process vendor if data are to be developed. These approaches are not reasonable until a Level 1 environmental assessment data gathering campaign is completed and these data show the need for treatment of the particular solid wastes. Detailed characteristics of the solid wastes and their leaching properties are not available for coal conversion systems. This information would normally be collected during the Level 1 environmental assessment. Some additional testing is suggested in the report to supplement the existing S/A procedures.

CAD investigators will require a fairly thorough familiarity with the SASS train operating manual, with IERL S/A procedures manuals, and with selected analytical procedures contained in Standard Methods(1).

SECTION 2

WASTEWATER METHODOLOGY

2.1 BACKGROUND

The Control Assay Development (CAD) program for wastewaters is intended to provide an initial evaluation of selected treatment processes and their applicability to coal conversion aqueous process wastes. CAD testing equipment and procedures have been designed for mobility and ease of operation in the field, to enable technicians to perform screening operations at a plant site and provide samples for analysis by IERL Level 1 analysis procedures.

Figure 1 shows the test sequence which will be performed on a composite sample taken at the plant. A 400-liter composite sample is required to provide sufficient quantity for all screening tests and analyses. Process streams which are to make up the composite sample are first analyzed for phenol, ammonia, cyanide and sulfide content and treated to remove these contaminants prior to compositing. The purpose of byproduct removal (when required) is to render the sample more representative of a commercial-size plant wastewater, where pollutants present in high concentrations will have typically been recovered as marketable byproducts. Floating oil and scum will also be removed from the sample at this point.

The recommended screening procedures are not intended to provide scale-up design data for a treatment plant, but rather, will indicate the potential applicability of a particular treatment process and provide information to be used as a basis for further studies. The tests have been limited to those treatment technologies which in actual practice (a) have proved the most successful, (b) are most universally applied, and (c) can be accomodated in a CAD mobile test facility.

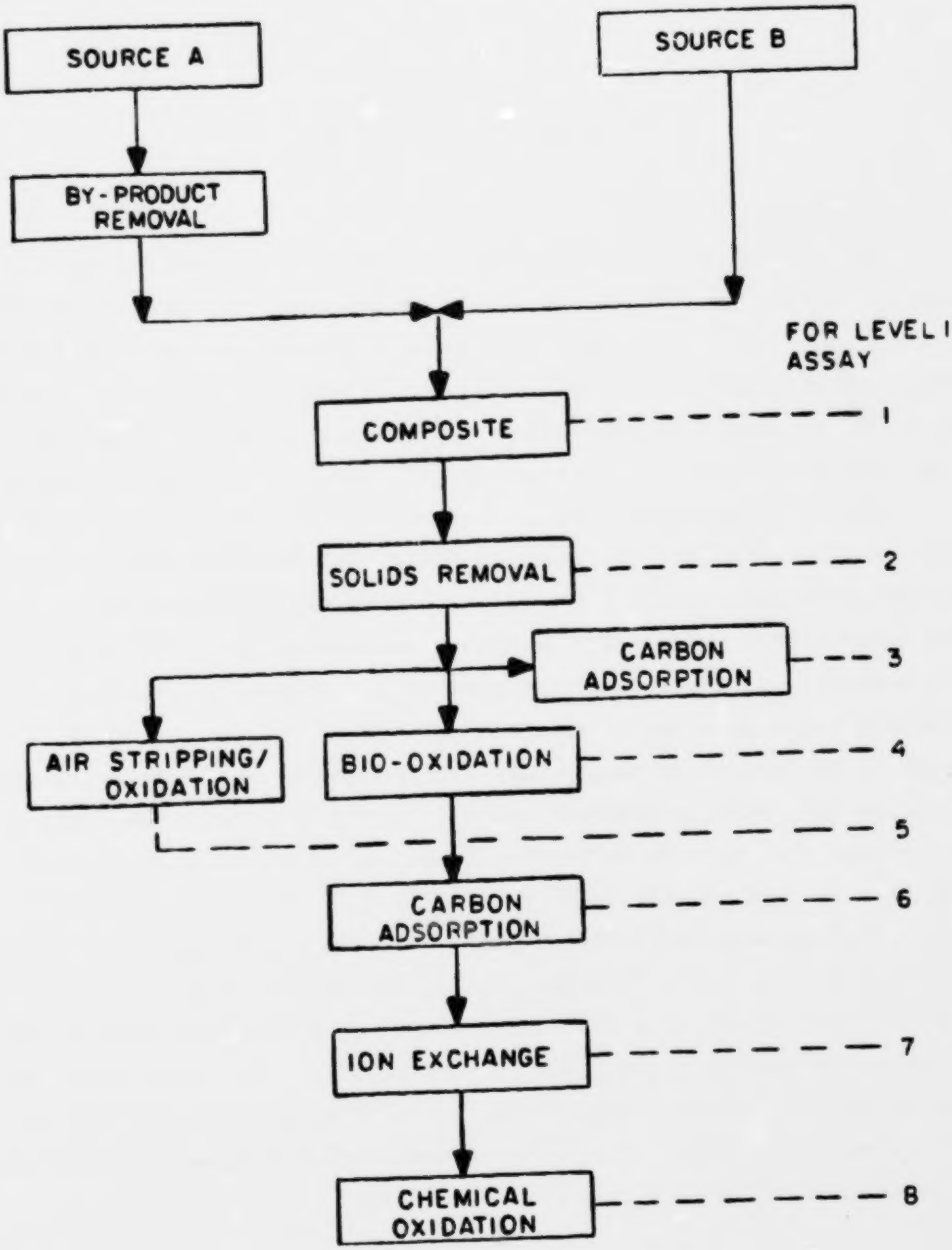

SOURCE A
SOURCE B
BY-PRODUCT REMOVAL
FOR LEVEL I ASSAY
COMPOSITE
1
SOLIDS REMOVAL
2
CARBON ADSORPTION
3
AIR STRIPPING/ OXIDATION
BIO-OXIDATION
4
5
CARBON ADSORPTION
6
ION EXCHANGE
7
CHEMICAL OXIDATION
8

Figure 1. Wastewater test sequence.

Various types of wastewater generated in coal gasification and liquefaction processes are:

1. Process Wastewater,
2. Coal Pile Runoff,
3. Process Area Storm Water Runoff,
4. Cooling Tower Blowdown,
5. Boiler Blowdown, and
6. Water Treatment Blowdown.

Of these, process wastewater has the most pollutants and, therefore, requires the most serious attention. Tables 1 and 2 illustrate the different sources and characteristics of process and other wastewaters from coal gasification (low to medium Btu) and liquefaction processes, respectively. The process wastes contain various pollutants including: suspended particles, phenols, tars, ammonia, cyanide, thiocyanates, sulfides, oils, light hydrocarbons, chlorides, other dissolved organics and inorganics. The pollutant concentrations could be very high, resulting in high Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). In addition, the process wastewater will contain heavy metals originating in the feed coal.

Process area runoff is a fugitive emission and, therefore, requires collection and equalization. It is expected to contain most of the pollutants present in process wastewater, and for this reason, is frequently treated together with process wastewater.

Coal pile runoff characteristics are dependent on the type of coal used in the plant. This wastewater will contain dissolved organics leached from coal and coal fines.

Cooling tower blowdown contains dissolved solids, suspended solids, corrosion inhibitors and bacteriacides. Through leaks in heat exchangers, cooling tower water can become contaminated with process liquors.

The recommended control assay screening operations are potentially capable of removing dissolved organics (both biodegradable organics and biorefractory organics), suspended solids, phenol, cyanide, ammonia, sulfide and other pollutants listed above to acceptable levels.

Numerous treatment processes are available for the control of pollutants, several affecting more than one pollutant. Table 3 lists various wastewater treatment technologies and the pollutants affected by them.

TABLE 1. COAL GASIFICATION PLANT WASTEWATER SOURCES AND CHARACTERISTICS

Process Module	Source	Contaminant
Coal Pretreatment and Storage	Coal-pile runoff; coal crushing and cleaning waste	Suspended Solids; dissolved organics
Gasifier	Ash quench/sluice water	Suspended solids; dissolved inorganics
Particulate Removal; Gas Quenching and Cooling; Acid Gas Removal	Process condensate; unrecoverable solvent	Suspended solids; non-emulsified oils; dissolved organics and inorganics; spent solvent
Cooling Tower	Blowdown	Suspended solids; dissolved organics and inorganics (volatiles and salts)
Utility System	Blowdown	Dissolved inorganics; suspended solids
Organics Separation	Process condensate	Suspended solids; dissolved organics and inorganics
Wastewater Treatment	Sludges	Semisolids

TABLE 2. COAL LIQUEFACTION PLANT WASTEWATER SOURCES AND CHARACTERISTICS

Module	Source Description	Wastewater Stream	Constituents
Coal Preparation	Coal storage piles, crushing and grinding operations	Storm water runoff	Suspended particles, dissolved solids
Hydrogenation	Cooling and quenching operation	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Pyrolysis and Hydrocarbonization	Cooling and quenching	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Hydrotreating	Condensing overhead vapors	Condensate	Phenols, ammonia, sulfides
Synthesis Gas Generation	Cooling and quenching operation	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
	Shifting Operation	Condensed unreacted water	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Catalytic Synthesis	Condensing overhead vapors	Condensate	Phenols, ammonia, sulfides
Phase Separation	Two or three stage pressure reduction	Condensate from overhead condenser	Oils, light hydrocarbons, phenols ammonia, dissolved sulfides
Fractionation	Cooling overhead vapors	Condensate	Light hydrocarbons, dissolved salts
Gas Cleaning	Absorption and regeneration operations	Purge Flows	Dissolved sulfides in gas removal solvent
Hydrogen Generation	Cooling and quenching operation	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides, and chlorides
	Shifting Operation	Condensed unreacted water	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Supercritical Gas Extraction	Char quenching operation	Foul water from quench	Phenols, tars, ammonia, thiocyanates, sulfides and chlorides
Auxiliary Systems and Utilities	Cooling towers and boiler	Blowdown	Dissolved solids
	Plant yard area	Storm water runoff	Suspended particles, dissolved solids, traces of phenols, oils and tars

TABLE 3

TREATMENT TECHNOLOGIES AVAILABLE FOR SPECIFIED POLLUTANTS

POLLUTANT	AVAILABLE TREATMENT PROCESSES
A. Dissolved Organics	
1. Undifferentiated	Bioconversion: Fixed Growth Trickling Filtration Rotating Biological Contactor Dispersed Growth Activated Sludge High Rate Conventional Extended Aeration Contact Stabilization Aerated Lagoon Aerobic (completely mixed) Facultative Anaerobic Lagoon
	Adsorption, Activated Carbon Granular Powdered Liquid-Liquid Extraction Irrigation Thermal Combusion Distillation Stripping (air or steam) Membrane Separation Ultrafiltration
	Chemical Oxidation or Reduction Freezing
2. Oil	Bioconversion Adsorption, Activated Carbon
3. Phenol	Oxidation (by ozonation or chlorination) Bioconversion Adsorption, Activated Carbon Extraction

TABLE 3. (Continued)

B. Suspended Solids	Separation - Sedimentation Filtration Granular Bed Pre-coat Microscreening Membrane Separation Ultrafiltration Flotation
	Pre-Treatment - Coagulation Flocculation
C. Dissolved Solids (Primarily inorganic, plus TSS)	
1. General (heavy metals, salts, some organics, others)	Precipitation Ion Exchange Electrolysis Metal Replacement Freeze Crystallization Reverse Osmosis Evaporation Electrodialysis
2. Heavy Metals	Precipitation Ion Exchange
3. Cyanide	Alkaline Chlorination Ozonation

TABLE 3. (Continued)

4. Nutrients	
a. Nitrogen	Bioconversion, Aerobic (Uptake of TKN) Bioconversion, Anaerobic (denitrification) Ion Exchange Stripping (of ammonia, by air or steam) Breakpoint Chlorination (of ammonia)
b. Phosphorus	Bioconversion, Aerobic Ion Exchange Precipitation
D. pH/Alkalinity/Acidity	Neutralization with acid or alkali
E. Floating Substances	
1. Solids	Surface Skimming
2. Oils	Surface Skimming
3. Foam	
F. Oil Emulsions	Emulsion-breaking (by steam, acid, alum,or iron salts, or commercial emulsion breakers)
G. Coarse Solids	Screening Sedimentation
H. Bacteria	Chlorination Ozonation Irradiation
I. Color	Chemical Oxidation or Reduction Bioconversion Activated Carbon

The pretreatment and basic unit operations to be used under CAD test work and the pollutants affected by them are:

Pretreatment Unit Operations	Pollutants Affected
1. Extraction	Phenol
2. Stripping	NH_3, H_2S,
3. Chemical Reaction (for Specified Pollutants)	Cyanides and Sulfides
Basic Unit Operations	
4. Filtration	Suspended and dissolved solids, and suspended/emulsified oil
5. Biological Oxidation	Dissolved organics
6. Activated Carbon Adsorption	Dissolved organics
7. Ion Exchange	Dissolved solids, heavy metals

Gravity oil separation is not included above because standard CAD procedures will permit raw samples to sit in their containers for sufficient time for oils and oily scum to float. Only subnatant wastewater will be used for test purposes.

Two basic treatment methods exist for the removal of dissolved organics, both having considerable versatility: biological conversion, and carbon adsorption.

Biological treatment in conjunction with various physical/chemical methods, is the most widely practiced treatment method for wastes containing dissolved organics. It will continue to play a key role in industrial waste treatment for the foreseeable future. Activated carbon adsorption is expected to be employed with increasing frequency for removal of bioresistant dissolved organics.

Both biological treatment and activated carbon adsorption have fundamental limitations. Some organic materials are non-biodegradable (or may degrade very slowly) and certain types are toxic to the biological organisms. Similarly, some organic materials, particularly low molecular weight compounds, are not easily adsorbed on carbon. Fortunately, there frequently is considerable overlap in the applicability of biological treatment and carbon adsorption. Many refractory compounds can be adsorbed, and many non-adsorbable compounds are biodegradable. There are, of course, exceptions where either or both of these processes will not be effective.

The range of available technology is much broader for the removal or control of other pollutants such as suspended solids, oil, heavy metals, cyanide, and phenol. It includes numerous chemical and physical processes such as: clarification, filtration, chemical coagulation and filtration, precipitation, ion exchange, ozonation, stripping, neutralization, dissolved air flotation, and oil separation by gravity. Frequently, one or more of these processes must be employed as a specialized pretreatment method on segregated process wastestreams to render the stream compatible for combined treatment by downstream processes. Cyanide removal (by alkaline chlorination), dephenolization (by solvent extraction or adsorption), and ammonia stripping are examples of pretreatment applications.

Since detailed waste characteristics of the samples may not be known, the unit operations selected are inherently designed to affect as many types of pollutants as possible. To test the effectiveness of these unit operations, effluent samples from them have to be analyzed by Level 1 Sampling/Analysis (S/A) protocols. This could create a large number of samples for analysis, if no limit is placed on the number of unit operations and raw samples. To place a reasonable boundary on the amount of test work required, the following procedural logic has been followed:

1. Although a large number of treatment processes/operations were initially considered, only a relatively few, broad based, generic-type technologies are included in the CAD test sequence (Figure 1).
2. Three of these unit operations are used for pretreatment of the different raw samples, if these pretreatments are found to be necessary by simplified field analysis. The remaining unit operations are used to test a composite wastewater prepared by mixing pretreated and/or raw samples. Compositing of wastewaters is quite typical in real-life waste treatment situations.
3. To concentrate investigative efforts on important problem areas, the composite for CAD screening procedures is limited to process wastewaters only (e.g., no cooling tower blowdown), unless substantial over-riding circumstances are present.

It is assumed that the CAD field team members will have a technical background in the environmental field, have a basic knowledge of chemical principles and be quite familiar with standard laboratory procedures. The CAD field crew is required to perform a number of analyses on-site when preliminary results are required to establish subsequent operating parameters.

2.1.1 Sampling Procedures

IERL Level 1 sampling procedures and standard practices will be used as a guide by the CAD team. These are discussed in "IERL-RTP Procedures Manual: Level 1 Environmental Assessment," Chapter V (2). It is recognized that CAD procedures may require modifications to the IERL methods in order to facilitate the larger sample size. For example, a stream which would normally be sampled with a dipper to obtain 10 liters may require a pump to obtain 400 liters. Stainless steel drums become the sample containers, rather than glass or plastic bottles. When modifications to Level 1 procedures are necessary, general recommendations regarding materials of construction and equipment cleaning have been suggested.

Procedures for handling the final 10-liter sample from each screening operation will be in accordance with the IERL manual.

Flow measurement of each stream which will be included in a composite sample is particularly important. Preparation of the composite sample is described in Section 2.3.

2.1.2 Sample Analysis

A 10-liter sample will be removed from each of the screening operations indicated in Figure 1. This volume is required by Level 1 analytical procedures for water organic and inorganic analyses. An additional 15 liters will be required for modified bioassay testing of the composite sample and the final effluent sample.

For purposes of defining field analytical responsibility, it is assumed that the CAD team will be working independently, but concurrently with a Level 1 S/A assessment team at the site. The Level 1 team will support the handling, preparation and analytical requirements for samples generated by the CAD team. On the surface, this approach is felt to offer the most cost effectiveness and will avoid the duplication of mobile laboratory facilities required for selected testing that must be conducted on site. (Future experience, however, may dictate otherwise, since the operating schedules/timetables of both the CAD and S/A teams may preclude their being on site for the same simultaneous period. In that event, the CAD laboratory facility's capability will have to be enlarged to the extent necessary for field handling of samples in accordance with IERL Level 1 S/A procedures.

The approach suggested above does not preclude the CAD team from performing limited analyses for the purpose of characterizing waste streams to guide in the selection of optimum operating parameters for CAD treatment unit operations. The supplemental analytical tests employed in CAD are relatively simple and inexpensive, and are described in the applicable methodology sections.

2.2 PRETREATMENT

2.2.1 General Comments

Wastewater streams encountered during CAD testing are expected to contain phenolic compounds, ammonia, sulfides and cyanide. These materials should be present in large enough quantities to make their recovery economical in a full scale plant; however, pilot plant operations may not be able to afford the capital investment for recovery equipment. Since it is expected that CAD testing procedures will, at least initially, be employed using wastewater streams produced by pilot plants, it becomes necessary to pretreat these samples in order to simulate the characteristics of the waste effluent that would be expected from a full-scale plant.

The analytical effort expected of the field team members is not extensive for any of the CAD testing. However, some analyses must be performed to evaluate the need for pretreatment and the degree of surrogate pollutant removal after a sample is processed through a pretreatment step.

The individual streams used to make up the composite sample will be analyzed using inexpensive test kits and a decision will be made by the CAD team leader as to which streams will be subjected to byproduct removal treatment before compositing. Because of the variation in flow rates and composition of the waste streams expected in different plants, it is not possible in this Section to specify exact equipment sizes or times required for byproduct removal. Each plant will present a new set of circumstances which must be evaluated before the screening procedures are commenced. A suggested maximum concentration for each species is listed in the individual write-ups in this Section. After byproduct removal and compositing, the sample should be analyzed to determine the effectiveness of any pretreatment steps employed, and also to insure that the composite sample meets the acceptable limits for the components in question.

Three of the four byproduct removal procedures are highly pH dependent: cyanide, ammonia, and hydrogen sulfide. When a waste sample is encountered which requires removal of more than one of these byproducts, a representative aliquot is tested as a side study to determine if it is possible to perform all the procedures in a single container by beginning with a higher pH and adjusting towards the final goal for the composite sample of about pH 7.0. If not, then the byproduct removal steps will have to be performed individually.

2.2.2 Phenol Removal

2.2.2.1 Introduction--

Liquid-liquid extraction removes phenol from a wastewater by contacting the stream with an organic solvent. The solvent should have a high affinity for removing phenol from water, be mutually immiscible with the water, have a significant difference in density from the water, have a reasonably low viscosity, and be low in cost. In most commercial applications, employing various methods of countercurrent contacting, approximately 99 percent of the phenol can be removed from a waste stream.

Solvents which have been used for phenol removal include benzene (or light oil), isopropyl ether, tricresyl phosphate, and other proprietary commercial solvents. Isopropyl ether is suggested for CAD work.

For all subsequent discussions regarding specific CAD testing, a basic presumption is made (and hereby emphasized) that the investigators will be cognizant of, and will employ, proper safety precautions and equipment when handling the samples and while performing the tests.

Several extractor types are capable of performing the required intimate contacting and subsequent separation. The Podbielniak centrifugal countercurrent extractor, which combines the advantages of a sieve column and a centrifuge, is suggested for CAD work. This compact unit has been applied previously to the dephenolization of waste streams; and removal efficiency is in the range of 95% or better, depending on the affinity of the solvent for phenol.

The Podbielniak extractor is constructed with a series of concentric "bands" perforated with many holes. When the machine is rotated (up to several thousand r.p.m.), the heavy liquid is thrown outward by centrifugal force, while the light liquid is displaced inward. This action causes a series of countercurrent "contacts" as the fluids pass through the holes, thereby producing multiple-stage extraction.

2.2.2.2 Summary of Method--

A wastewater sample is pumped into the extractor at a rate of 1 gpm or less. Simultaneously, the solvent is pumped into the other extractor inlet at a variable flowrate of up to 1 gpm. The locations of the inlets for the respective liquids are determined by their relative densities (the heavier fluid enters the center of the extractor, the lighter fluid enters the outside ring of the extractor).

Phenol removal will vary with the change in solvent-to-water ratios, which can be varied by manually opening or closing the valves in each line.

2.2.2.3 Apparatus--

Liquid-liquid extraction unit (Podbielniak or equivalent)
Phenol test kit (Hach or equivalent)
pH meter
Pumps(2) variable speed to 1 gpm
Sample containers
Series of volumetric flasks (1000,500,250,100,50,10 ml)*
Assorted pipets*

2.2.2.4 Reagents--

Isopropyl ether

2.2.2.5 Preparation--

Analyze the individual stream samples collected for preparation of the composite sample for phenol using the colorimetric test kit. Make dilutions, as required, for samples with high phenol concentrations. Streams containing concentrations which will produce a level of greater than 250 mg/l of phenolic compounds in the composite sample will be subjected to the extraction process.

2.2.2.6 Procedure--

Set up the apparatus as shown in Figure 2. Mix all sample streams requiring treatment in a suitable container. Start the flow of sample and solvent to the extraction unit. The sample flow should be approximately 1 gpm and solvent flow 0.5 gpm. Continue operation until all of the sample has been processed by the extractor. Analyze the effluent from the reactor for phenol, again using the colorimetric test kit. Repeat the extraction procedure, if necessary, until phenol concentration has been reduced to the specified level.

2.2.3 Hydrogen Sulfide and Ammonia Removal

2.2.3.1 Introduction--

Hydrogen sulfide and ammonia can be removed from wastewater by differential batch distillation. This process involves sparging air or steam into a drum containing the wastewater until the concentration of the hydrogen sulfide and ammonia has reached a predetermined level.

---

*This laboratory glassware will be required for all analytical determinations and is not repeated in subsequent sections.

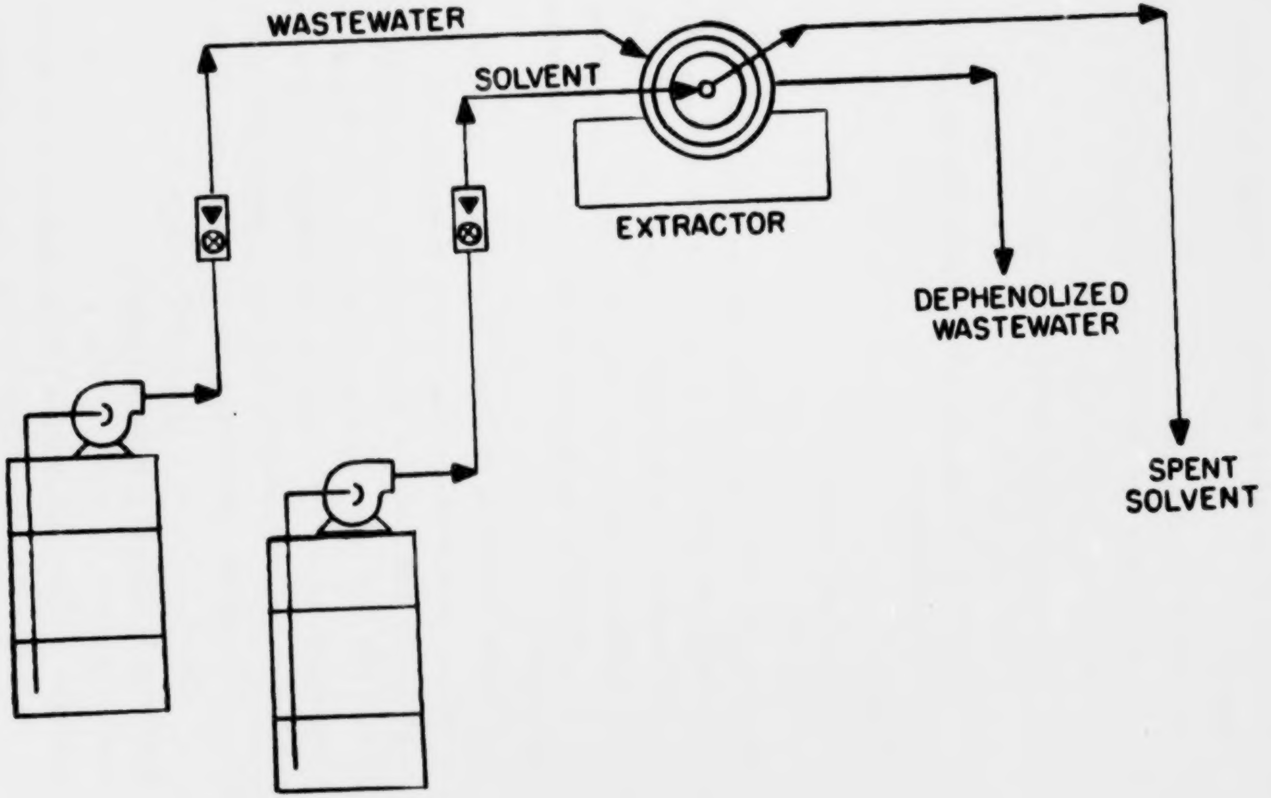

WASTEWATER
SOLVENT
EXTRACTOR
DEPHENOLIZED
WASTEWATER
SPENT
SOLVENT

Figure 2. Phenol extraction apparatus.

The pH of the system has an effect on the ease of removal of hydrogen sulfide and ammonia. If the pH of the wastewater charge is adjusted to about 7, hydrogen sulfide will be liberated easily by the sparged air. Ammonia stripping is optimal when the pH of the wastewater charge is raised to about 11 (accomplished by addition of sodium hydroxide).

A high percent removal rate of hydrogen sulfide can be accomplished in a matter of minutes. Theoretically, with perfect mixing, a 98 percent ammonia removal efficiency from a 55-gallon wastewater charge at 20°C using 60 cubic feet per minute of sparged air will be accomplished in about 13 hours. If the wastewater temperature is increased to about 60°C, the time requirements will drop to less than 3 hours. Therefore, with the addition of a heat source and a proper air diffuser device, a high percent removal of ammonia will take place in a reasonable amount of time.

2.2.3.2 Summary of Method--

Air is compressed and pumped to the bottom of a drum which contains the composite wastewater sample. The air is discharged through a sparger mechanism which diffuses the air bubbles through the liquid, allowing intimate contact and mass transfer from the liquid to the air. A submersible heater is used to heat the sample to approximately 60°C during the sparging operation.

2.2.3.3 Apparatus--

Sample containers
Immersible heater
Air compressor (capacity 60 cfm) and tubing
Air diffusion mechanism
Hydrogen sulfide test kit
Ammonia test kit
Thermometer (0°-100°C)

2.2.3.4 Reagents--

NaOH - 50% solution
H_2SO_4- 10 Normal

2.2.3.5 Preparation--

Analyze the sample for ammonia and hydrogen sulfide. The acceptable limit in the composite sample for ammonia is 500 mg/l. Position the immersible heater in the sample container and bring the sample temperature to 60°C. Adjust the pH of the solution to 11 or greater.

2.2.3.6 Procedure--

After the sample has reached 60°C begin aeration. Analyze the sample every hour until an acceptable ammonia level has been reached. At this point, the pH is adjusted to 7.0 and aeration is continued until the sulfide has been removed to a constant concentration level.

(Note: If cyanide is also to be removed from this sample, perform this operation before lowering the pH. See Section 2.2.4.

2.2.4 Cyanide Removal

2.2.4.1 Introduction--

Complete destruction of the cyanide ion can be accomplished with chlorine gas in an alkaline solution (pH 10 or greater) at room temperature. During the chlorination step, heavy metals that accompany cyanide can precipitate as hydroxides and ferro or ferricyanides. The iron compounds react very slowly with chlorine, and for this reason, vigorous agitation is required in the process.

Addition of sodium or calcium hypochlorite will also completely destroy cyanide without the need for the addition of caustic. Vigorous agitation, however, is also required with this method.

2.2.4.2 Summary of Method

Sodium hypochlorite is added to the sample and vigorously agitated to destroy cyanide.

2.2.4.3 Apparatus--

Sample container

Air compressor and diffusion mechanism or laboratory mixer to provide agitation.

2.2.4.4 Reagents--

Sodium hypochlorite

2.2.4.5 Procedure--

Place the sample to be treated in an appropriate size container and begin agitation. Add sodium hypochlorite and agitate until the cyanide level reaches 1 mg/l or below. (If this level cannot be achieved with hypochlorite alone, adjust the sample to pH 10^+ with caustic and continue treatment until the specified cyanide concentration is reached.)

2.3 PREPARATION OF COMPOSITE SAMPLE

Demonstration and commercial size synfuel plants will normally contain a central wastewater treatment facility wherein many process waste streams are combined, mixed and equalized prior to entering the various treatment steps. A Level 1 S/A assessment would be concerned primarily with the treated effluent stream being discharged. In these cases, CAD may not be required unless data have been obtained that indicate unsatisfactory performance of the plant.

Where process wastes are not being treated in a central facility, the individual streams must be composited to simulate the combined feed to a treatment plant. This situation might be encountered in pilot plants. Knowledge of the process and/or similar conversion processes is essential to enable the CAD team to select individual waste streams that will most likely eventually be combined for subsequent treatment.

A data sheet for recording information needed to prepare a composite sample is attached as Table 4. The composite will be a mixture of each stream in proportion to its flow. Following is an example of this calculation:

Assuming a 400-liter sample requirement,

Stream No.	Flow Rate	Proportional Volume Calc.
1	100 gpm	$\frac{100}{370}$ x 400 L = 108 L
2	90 gpm	$\frac{90}{370}$ x 400 L = 97 L
3	150 gpm	$\frac{150}{370}$ x 400 L = 162 L
4	30 gpm	$\frac{30}{370}$ x 400 L = 33 L
	370 gpm	400 L

The composite sample should be used in the next CAD step (Solids Removal) as soon as possible. Streams requiring pretreatment should be handled first, and added to freshly obtained samples from other sources that do not require preliminary handling.

Two 55-gallon stainless steel drums, equipped with agitators, will normally be adequate to composite the sample quantity required for subsequent pre-screening and screening operations. The drums must be fitted with tight covers to prevent contamination from airborne dust, etc.

TABLE 4. DATA SHEET FOR COMPOSITE SAMPLE

Composite sample volume required: ____________

Date/time prepared: ___________________________

Stream No.	Source	Date/time Sampled	Flow Rate	Type Pretreatment	Date/time Pretreated	Final Temp.	Final pH	Proportional Volume Calculations

2.4 SCREENING PROCEDURES

2.4.1 Solids Removal

2.4.1.1 Introduction--

Some type of solids removal is usually required in industrial wastewater treatment applications. The three basic types of solids separation commonly employed are gravity separation, physical straining, and filtration through granular media. These processes are often combined with chemical coagulation and flocculation in order to produce higher solids removal efficiencies. Solids removal can be utilized as a polishing step to meet effluent requirements. It is also used as a pretreatment step to assist subsequent unit processes by reducing the solids loading they must handle. This latter approach will be taken in the CAD methodology. The composite sample will be filtered without benefit of chemical treatment in order to avoid unnecessary altering of the sample's characteristics.

2.4.1.2 Summary of Method--

Solids are removed from the composite wastewater sample by a combination of sedimentation and pressure filtration through a cartridge filter. The effluent from the filter is collected and will be used in subsequent CAD testing procedures.

2.4.1.3 Apparatus--

Centrifugal pump with stainless steel or teflon coated liquid contacting surfaces (Capacity: 5 gpm)

Cartridge filter holder - stainless steel or polypropylene with replacement cartridges (75-micron Serfilco cartridges or equivalent)

Flexible teflon tubing 1/2-inch I.D. and pump fittings

Sample containers to hold a 400-liter composite sample (stainless steel or polypropylene)

2.4.1.4 Reagents--

None required.

2.4.1.5 Preparation--

The sample should remain quiescent in the storage container for at least one hour to allow settling of larger particles. Floating oil and scum should be removed from the sample at this time.

2.4.1.6 Procedure--

Attach the filter cartridge to the pump and begin the sample flow through the filter. Adjust the flow rate to approximately 1 gpm. If the filter becomes clogged during the run, stop the feed pump and replace the cartridge according to the manufacturer's instructions. Collect the effluent in the sample container and reserve for further testing procedures. Submit a 10-liter sample for Level 1 analyses.

2.4.2 Carbon Adsorption

2.4.2.1 Introduction--

Activated carbons are made from a variety of materials including wood, bituminous coal, sawdust and petroleum residues. The activation process develops a complex pore structure on the surface of the carbon granules. It is this porous structure which encourages adsorption - the phenomenon by which molecules adhere to a surface with which they come in contact. Usually removal of organics by activated carbon is the result of van der Waal's forces - a physical attraction between molecules.

Activated carbon preferentially adsorbs high-molecular weight organics and/or non-polar substances from aqueous solutions, and is frequently used to remove odor, taste and color from water.

When the organic loading is too low to support a biological system, or when the organic materials in a waste stream are toxic to bacteria, carbon can be used as an alternative treatment system. Carbon is sometimes used after biological treatment to serve as a polishing step to achieve greater organic removal.

Activated carbon may be used in a batch or column operation; however, the most efficient application is in continuous-flow, packed-bed columns. In packed beds, the carbon remains stationary while the wastewater is introduced either from the top or bottom of the column. The column itself is a vertical, cylindrical pressure vessel. It is of sufficient height that the required depth of carbon represents only 50 to 60% of the total internal height. This allows for bed expansion during backwash operations. The column is provided with an internal screen support which holds the carbon bed above the bottom of the vessel.

A common variation of the packed-bed design is the fluidized bed. In this type of column, the wastewater is introduced at the bottom of the column at a flow rate high enough to slightly expand the carbon bed. This design is useful when moderately sized solids are present in the wastewater.

Another variation of the packed-bed design is the moving or pulsed bed adsorber. In columns of this type, the wastewater is fed to the column from the bottom and flows upward through the carbon bed. A storage vessel located on top of the column holds fresh or reactivated carbon. This fresh carbon is fed to the top of the column at intervals based on the contaminant loading and the adsorptive capacity of the carbon. As carbon is added at the top of the column, an equal amount of spent carbon is discharged from the bottom of the column and sent for regeneration. This design greatly reduces the complexities of changing the carbon in the column and allows uninterrupted operation of the column.

All types of columns experience a gradually increasing pressure drop across the system due to a build-up of particulate matter in the filter. Because of this gradual plugging of the column, a backwashing step becomes necessary when an unacceptable pressure drop is experienced. Obviously, pretreatment of the wastewater to remove suspended particles will allow for a longer column run between backwashing steps. The suspended solids level in the water to be treated determines whether a pretreatment step is necessary; however, for most wastes this step will increase the efficiency of the column enough to be warranted.

Variables which affect the adsorptive capacity of activated carbon include: type of carbon, pH of water to be treated, amount of contact time and temperature during contacting.

Activated carbon will be tested in CAD to determine if it can remove organic material from a wastewater sample. An isotherm test will first be performed to determine the approximate loading rate (amount of carbon required) and the effects of pH on organic removal. Continuous column operation will be used to process the composite sample.

Carbon adsorption column testing is performed twice in the CAD procedures. Referring to the flow scheme for wastewater (Figure 1), the methodology is applied after filtration, and following bio-oxidation. The column operation procedure is applicable to both cases, however, the isotherm test is only required for the first sample. The amount of carbon and optimum pH as indicated by this test is applicable in both cases. The two different column runs shall be identified as:

Carbon-1: Final treatment (after filtration)
Carbon-2: Intermediate treatment (in series between bio-oxidation and ion exchange)

2.4.2.2 Summary of Method--

A filtered wastewater sample is contacted for one hour in a standard shaking apparatus with seven different concentrations of activated carbon. Determination of TOC removal will indicate the adsorptive capacity of the carbon and the dose required for maximum organic removal. A second portion of filtered sample is further tested by contacting eight individual aliquots for one hour with the selected carbon dosage over the pH range of 4 to 11. Determination of TOC removal will indicate the optimum pH condition. The composite sample is then passed through a series of columns to remove dissolved organic material.

2.4.2.3 Isotherm Apparatus--

250-ml Erlenmeyer flasks with stoppers(16)
Eight place wrist-action shaker
Millipore filter assembly and 0.45-micron filters
1-liter vacuum flasks and vacuum source(2)
250-ml vacuum flask
100-ml graduated cylinder
pH meter
Filter paper - Whatman No. 42 or equivalent
Buchner type filter funnels
TOC analyzer
Triple beam balance, sensitivity to 0.1 grams

2.4.2.4 Isotherm Reagents--

H_2SO_4 - 1 Normal Solution
NaOH - 1 Normal Solution
Powdered activated carbon (ICI Darco 400 or equivalent)
Distilled Water

2.4.2.5 Isotherm Preparation--

Preparation of the activated carbon must be done at the home laboratory prior to the start of field testing.

1. Pulverize approximately 50 grams of granular activated carbon so that 95% will pass through a 325-mesh screen. Oven dry the pulverized sample for three hours at 105°C.

2. On an analytical balance, weigh the following amounts of carbon: 0.05, 0.1, 0.5, 1, 2, and 10 grams. Also weigh ten portions of a 5-gram amount.

3. Place each of the portions in marked containers (glassine envelopes) which can be sealed for transfer to the field.

2.4.2.6 Procedure--

1. Obtain two liters of composite sample and filter through Whatman No. 42 (or equivalent) to remove any suspended particulate matter.

2. Run TOC on an aliquot of this filtrate.

3. Mark eight Erlenmeyer flasks for identification and empty the preweighed carbon (0.05, 0.1, 0.5, 1, 2, 5, 10 gm) into the appropriate flasks. Care must be exercised to be certain that all the carbon is transferred from the container to the test flask. Flask No. 8 shall serve as the blank.

4. Measure 100 ml of filtered sample into each of the eight flasks. Place all flasks on the shaker apparatus and agitate for at least one hour. The flasks may be filtered and placed on the shaker at three to five minute intervals to allow sufficient time to filter each sample immediately after the prescribed contact time has elasped.

NOTE: Large doses of carbon may raise the pH of the solution with time. After 30 minutes on the shaker, the pH should be checked and readjusted to the initial value, if necessary.

5. After the contact time has elasped, filter the contents of each flask into a clean container. The high doses of carbon may require up to ten minutes of filtration time when filtered through the millipore system. To minimize filtration time, the sample may be filtered through a coarse filter (42 Whatman) before being filtered through the millipore filter.

6. Run TOC tests on all filtrates.

7. Tabulate the data as indicated on the sample data sheet (Figure 3). The residual waste material concentration, C, is obtained directly from the filtrate analysis. The amount adsorbed on the carbon, (total mg) is obtained by subtracting the value

of C from that of C_o, the influent concentration, and adjusting for sample size. Dividing X by M, the weight of carbon used in the test, gives the amount adsorbed per unit weight of carbon.

8. On log-log paper, plot X/M on the vertical axis (ordinate) against C on the horizontal axis (abscissa) and draw the best straight line through the points. See example Figure 3.

9. Extend the adsorption isotherm to the vertical line which represents the influent waste concentration. Where these two lines cross, read the X/M value on the ordinate. This will give the maximum possible loading of waste material expressed in milligrams/gram. (52 mg waste constituent adsorbed per gram activated carbon, in the example). It should be remembered that this loading can only be achieved if the carbon is brought into equilibrium with the influent waste stream. Calculate the waste loading to be applied to the columns during screening by the following formula:

$$W = \frac{(1)\ (Co)}{1000}$$

where W = Total waste load (grams)

1 = Volume of sample through columns (liters)

C_o = Waste influent concentration (mg/1)

$$W = \frac{(100\ 1)\ (712\ mg/1)}{1000\ mg/gm}$$

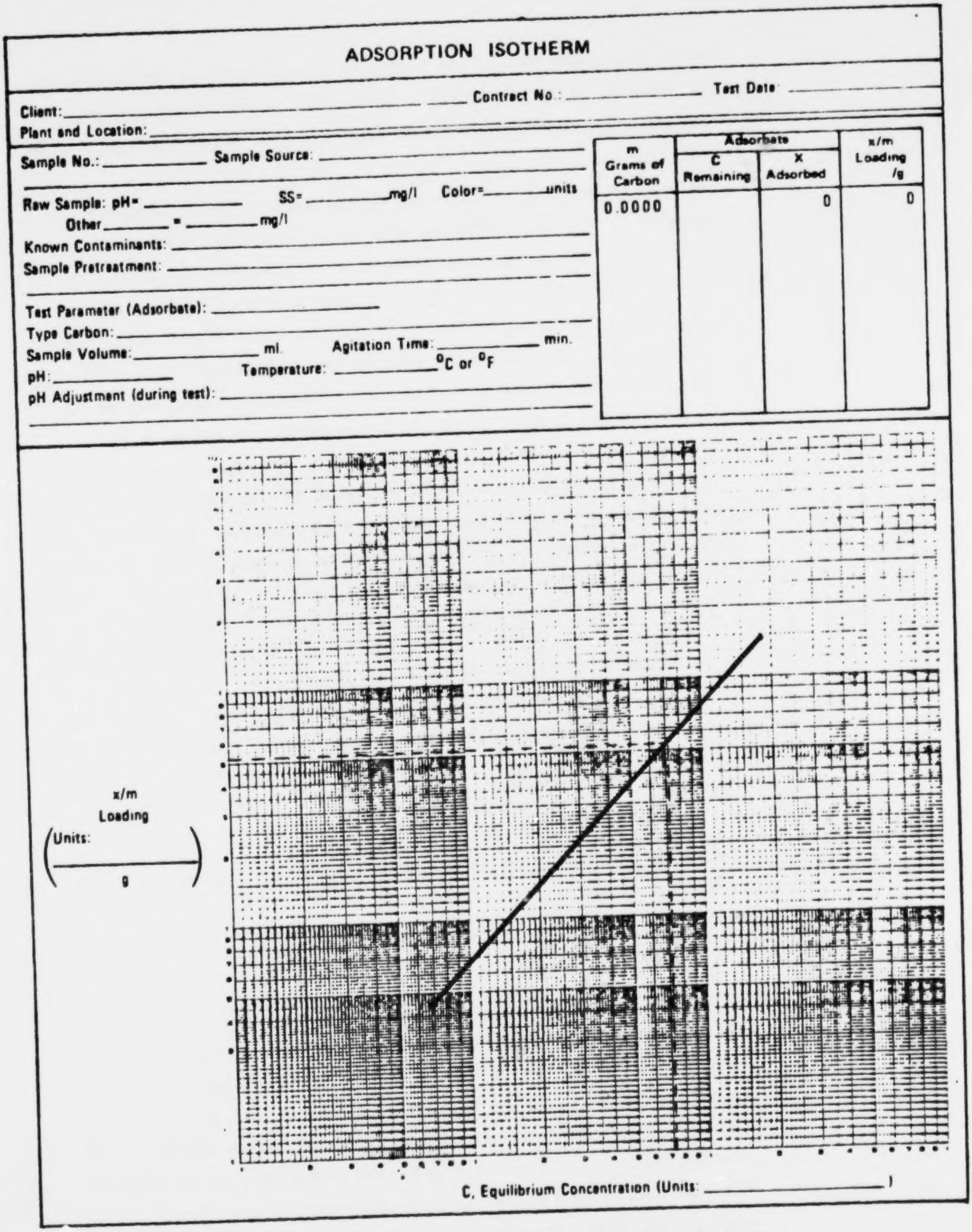
$$W = 71.2\ gms$$

Using the X/M value of 52 mg/gm, calculate the amount of carbon required to treat the waste.

$$52\ mg/gm = \frac{0.052\ gm}{gm} = 5.2\%\ loading$$

$$\frac{71.2}{0.052}\ gms = 1369\ gms\ carbon\ required = 3.0\ lbs.$$

10. Place the 5-gram portions of carbon into each of eight flasks. Adjust the pH of eight 100-ml aliquots of the filtered composite sample to pH 4, 5, 6, 7, 8, 9, 10, 11. Note and record any changes in the sample - i.e., evolution of gases, formation of precipitate, etc. Stopper the flasks and place on the shaker for one hour. Filter and analyze the samples for TOC, and plot pH vs. final concentration (TOC, mg/1). This graph will indicate the pH of most efficient carbon adsorption.



ADSORPTION ISOTHERM

Client: ______ Contract No.: ______ Test Date: ______

Plant and Location: ______

Sample No.: ______ Sample Source: ______

Raw Sample: pH= ______ SS= ______ mg/l Color= ______ units

Other ______ = ______ mg/l

Known Contaminants: ______

Sample Pretreatment: ______

Test Parameter (Adsorbate): ______

Type Carbon: ______

Sample Volume: ______ ml. Agitation Time: ______ min.

pH: ______ Temperature: ______ °C or °F

pH Adjustment (during test): ______

m Grams of Carbon	Adsorbate C Remaining	 X Adsorbed	x/m Loading /g
0.0000		0	0

x/m Loading (Units: / g)

C, Equilibrium Concentration (Units: ______)

Figure 3. Typical adsorption isotherm

2.3.2.7 Column Apparatus--

Four-foot glass columns, 3-inches in diameter, fitted with support screens to hold the carbon; end plate fittings are also required, and pressure gauges may be installed on each column. (See Figure 4).

Support structure for columns

Pump capable of uniform delivery rates of approximately 400 ml/min-gear, diaphragm, centrifugal, piston-type or cam finger pump.

Container for use as a sample feed reservoir - 40 gal. stainless steel or polypropylene.

Water Supply - Source of uncontaminated water for backflushing and charging the columns.

Portable pH meter

Sample collection container - 40-gal, stainless steel or polypropylene.

Graduated Cylinder - 5000 ml

Bucket - 2 gallon

2.4.2.8 Column Reagents--

Activated Carbon - granular 8 x 30 standard sieve size.

NaOH - 1-Normal Solution

H_2SO_4 - 1-Normal Solution

2.4.2.9 Column Preparation--

A. Assemble the apparatus as shown in Figure 4.

B. Charging the columns

1. Remove the top flange of the first column for filling and add approximately three feet of uncontaminated tap water. Measure the volume of water as it is added.
2. Make a carbon slurry in the 2-gallon bucket and pour slowly into the top of the column. Repeat this procedure until carbon has been added to a level of 3.0 feet. During addition of the slurry, occasional draining of the

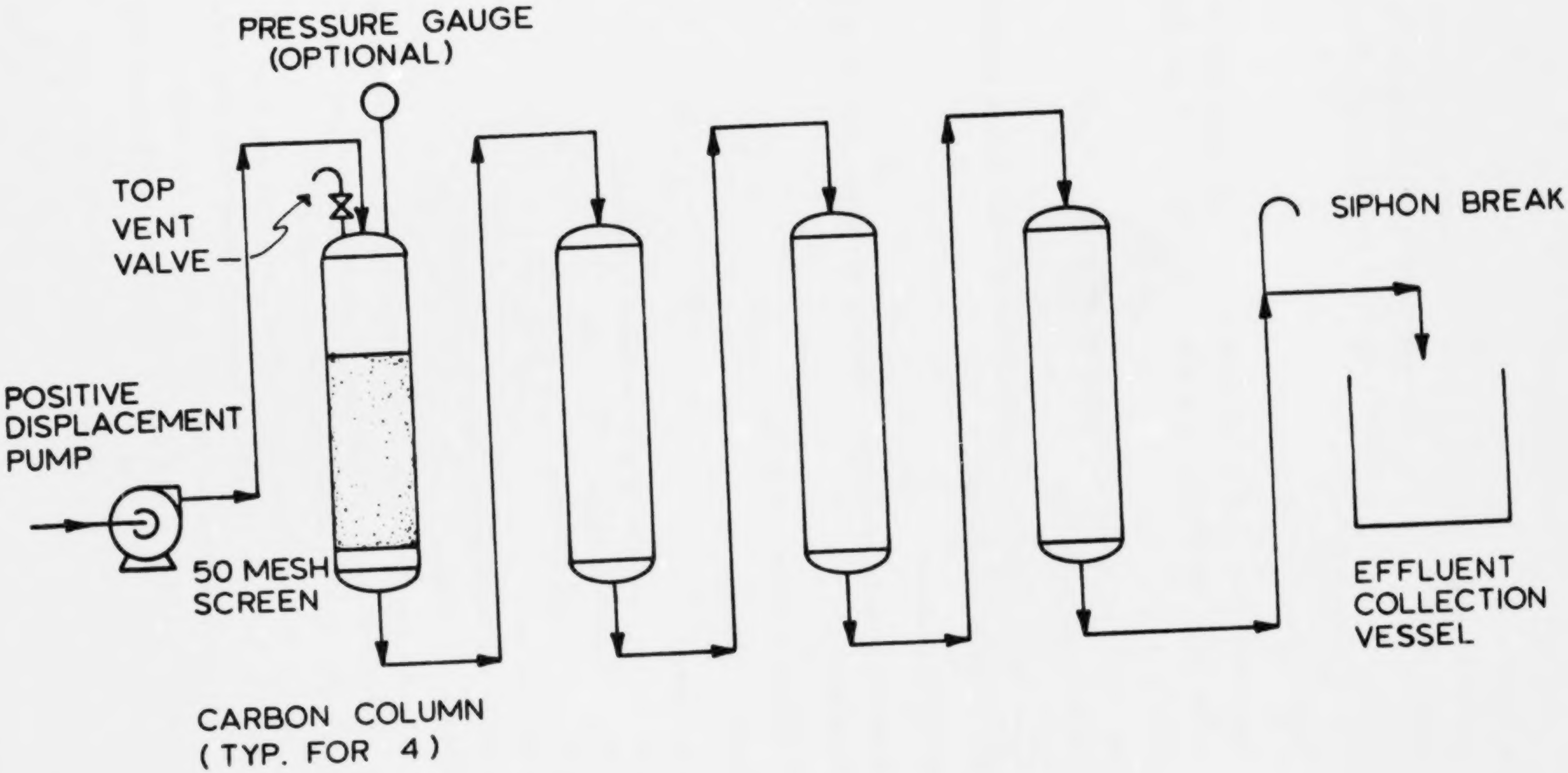

PRESSURE GAUGE
(OPTIONAL)
TOP
VENT
VALVE
POSITIVE
DISPLACEMENT
PUMP
50 MESH
SCREEN
CARBON COLUMN
(TYP. FOR 4)
SIPHON BREAK
EFFLUENT
COLLECTION
VESSEL

Figure 4. Carbon column apparatus.

excess water will be required to prevent overflowing the column. Measure and record the amount of water added with the slurry and drained from the columns for use in calculating the dilution factor.

3. Replace the top flange and repeat the charging procedure for each successive column.

C. Backwashing the columns

1. Attach the water supply line to the bottom of the first column.
2. Slowly start the flow up through the column and increase the rate until the bed has expanded to within three inches of the top of the column, allowing only the fine carbon particles to escape. Gently tap the column during backwashing to remove air pockets.
3. Stop the water flow to the column and adjust the level to 1 inch above the carbon.
4. Repeat the backwash procedure for each column.

2.4.2.10 Column Procedure--

1. With the effluent discharge valve closed and all top vent valves open, fill each column (except column one) with tap water to remove any air in the columns. Record the amount of water required.
2. Adjust the pump flow rate to 2 gpm/ft^2. With a 3-inch diameter column, this will be about 370 ml/min.
3. Begin feeding waste to the first column. When column 1 is completely filled with liquid, close the top vent and open the discharge valve and syphon breaker.
4. Begin running the waste through the columns at the constant rate specified above.
5. Collect the entire volume of effluent.

Measure the amount of sample collected. Record this amount and calculate and record the amount of dilution water used to charge the columns.

Carbon-1: Final Treatment - submit 10 liters for Level 1 analysis.

Carbon-2: Intermediate Treatment - save the effluent for use in CAD ion exchange screening.

2.4.3 Biological Oxidation

2.4.3.1 Introduction--

Biological oxidation is a unit process commonly used for removal of organics from industrial wastewaters. In this process, bacteria and other living organisms are used to break down organic compounds to simpler forms, and (in theory) ultimately to carbon dioxide and water. Methods of contacting the wastewater with the biological solids (sometimes called biomass or biota) vary according to wastewater flowrate, land area available and the desired percent removal of organics. Typical installations include trickling filters, aerated lagoons and activated sludge processes. An aerated lagoon is any basin in which biological organisms are allowed to grow and proliferate by aerating with addition of a feed material (dissolved organics in wastewater). Solids are kept in suspension and, therefore, the effluent solids concentration is equal to the solids concentration in the lagoon. In the activated sludge process, solids are allowed to settle in a clarifier and a portion of the solids is recycled to the aeration system. The excess solids produced by the system must be disposed of by other means. A trickling filter is a packed bed of media covered with a biological slime. The wastewater flows through the media and the organisms in the biomass assimilate and oxidize the organics in the water. Waste products such as CO_2, NH_3 and partially oxidized organics are carried off in the effluent. As the biomass grows thicker, those organisms close to the media surface are deprived of food and oxygen and thus become anaerobic. At this point, part of the biomass is sloughed off and the growing process begins again.

In order to obtain meaningful data from a pilot biological reactor, the microorganisms used in the system must be allowed to become acclimated to the wastewater for a period of several weeks. To meet this requirement, it will be necessary to send one member of the CAD field team to the plant site about one month prior to the actual control assay testing.

Laboratory results using a synthetic coal conversion wastewater indicate that a large percentage of organics can be removed by aeration alone. For this reason, two units will be run simultaneously to differentiate between removal of organics by air stripping/oxidation and by biodegradation.

2.4.3.2 Summary of Method--

The wastewater sample is treated by two systems - one containing previously acclimated microorganisms and the other having no biologically active seed. Both systems are aerated for 48 hours before removing a 10-liter sample for Level 1 analyses.

2.4.3.3 Apparatus--

Stainless steel containers (2) - each having a 55-gal. capacity.

Dissolved oxygen meter and accessories

pH meter and probe

Air compressor with tubing, air diffusion stones, and rotameters for flow measurement

Laboratory equipment for determination of suspended and volatile solids. (See Reference 1)

COD apparatus (See Reference 1)

Variable speed pump and tubing (0-5 gpm).

BOD apparatus (See Reference 1)

TOC Analyzer

2.4.3.4 Reagents--

NaOH - 1 Normal Solution
H_2SO_4 - 1 Normal Solution

Probe solutions for pH and dissolved oxygen meters
Anti-foaming agent
NH_4OH - 10% Solution
Na_2HPO_4 - 10% Solution

Reagents necessary for performing BOD and COD tests

2.4.3.5 Preparation--

During the preliminary plant visit, information concerning the waste streams which will make up the composite sample will be obtained by the CAD team leader. To avoid performing byproduct recovery steps on the waste which will be used only for acclimating the seed, the team leader must make a judgement, based on process knowledge, as to the procedure for preparing the acclimation mixture. In certain instances, for example, it may be possible to reduce byproduct contaminant levels by dilution of the sample rather than using the prescribed treatment procedures. This would limit the amount of equipment and effort required for seed acclimation to the point that it would be feasible for one person to perform this function. Waste treatment facilities in the vicinity of the plant should also be visited during the preliminary survey to gain information on types of activated sludges available locally.

2.4.3.6 Seed Acclimation--

Prior to the start of CAD screening, one team member will travel to the plant for the purpose of acclimating a seed. Duties during the three weeks will include:

1. Obtaining seed material from a local waste treatment plant;
2. Preparing the feed according to the instructions of the team leader;
3. Batch addition of feed to the unit using the fill-and-draw method; and
4. Monitoring the unit to determine approach of steady-state conditions.

Biological treatment of a waste sample is the most complex unit process which will be studied under the CAD wastewater program. For this reason, it is recommended that the field operators be thoroughly familiar with the techniques of start-up and operation of bench-scale, activated sludge biological reactors. An illustrative approach is presented below.

Obtain a 100-liter sludge sample from the secondary clarifier underflow (sludge return) line at a local activated sludge treatment plant and analyze this sample for suspended solids (SS) and volatile suspended solids (VSS). Ideally, this sludge would be obtained from a plant which normally treats coke oven or petroleum wastes; however, this will not always be possible and the alternative is to obtain sludge from a municipal sewage treatment plant. Also, a 100-liter sample of the clarified effluent will be obtained for use as a diluent to make up the initial reactor SS concentration.

The activated sludge sample must be placed under aeration as soon as possible after collection, and aerated vigorously to maintain a dissolved oxygen concentration of 2.0 mg/l or greater. It is also advisable to maintain aerobic conditions in the clarifier supernatant sample.

After determining the solids concentration in the return sludge sample, calculate the amount of sludge required to produce a suspended solids concentration of 5000 mg/l in the reactor based on a total volume of 150 liters. For example, 75 liters of sludge having a concentration of 10,000 mg/l of solids would produce approximately the required concentration when mixed with 75 liters of the clarifier supernatant sample. Mark the 150 liter (unaerated) liquid surface level on the inside of the reactor, so that water evaporation losses can be made up daily during the acclimation period.

Using the fill-and-draw method, the proper volume of feed is mixed with the sludge and aerated in an open container. After 24 hours, the aeration is stopped for one hour to allow settling of the solids, evaporative water losses (if any) are made up by filling the container to the fill mark with tap water, and then a supernatant quantity equal to the next day's feed volume is syphoned off. This process is repeated each day until the reactor has reached the final feed strength.

The feed strength will be increased each day for a period of fifteen days, at which time the system will be receiving the full waste load. There are two methods generally employed for increasing feed strength: logarithmic progression and arithmetic progression. Table 5 indicates the quantities of feed material to be added to the system.

Although either method of calculating the feed volume is acceptable, the logarithmic progression is regarded as being preferable insofar as the conversion to a new waste is done at a more gentle rate during the early portion of the acclimation period. Should the reactor performance demonstrate process stress during acclimation, rest the unit (aerate without feed) for 24 hours before resuming the feed schedule.

During the acclimation period the operator will monitor the performance of the system using the following analyses*:

Chemical Oxygen Demand (COD) - Daily on the feed and settled reactor supernatant

Biological Oxygen Demand (BOD) - Several days per week on feed and settled supernatant

Suspended Solids (SS) - Daily on the feed settled supernatant and on the aerating reactor contents (Mixed liquor)

---

* All analytical methods may be found in Reference 1.

TABLE 5

ACTIVATED SLUDGE SEED ACCLIMATION SCHEDULE

Day	Logarithmic Progression Percent of Total Volume	Logarithmic Progression Liters Added	Arithmetic Progression Percent Of Total Volume	Arithmetic Progression Liters Added
1	9	13	9	13
2	10	15	14	21
3	12	18	19	29
4	14	21	25	38
5	17	25	31	46
6	19	29	36	54
7	23	34	41	62
8	27	41	47	71
9	32	48	53	79
10	37	56	58	87
11	44	66	63	95
12	52	78	69	103
13	61	92	75	112
14	73	110	80	120
15	85	128	85	128

NOTE:

1. A "heel" volume of 15 percent is provided in the above calulations to allow space for the settled activated sludge.

2. At the start of the one-hour settling period (immediately after aeration has been stopped), the reactor volume should be made up to the 150-liter mark with tap water to adjust for any evaporative losses. The amount of water introduced should be recorded in the operating log book.

Volatile Suspended Solids (VSS) - Same as for SS

pH - Same as for SS (adjusted when necessary to maintain pH 6.0-8.0)

Dissolved Oxygen (D.O.) - Daily on the mixed liquor

Oxygen Uptake Rate (OUR) - Same as for D.O.

To determine nutrient requirements for the system the feed sample will be analyzed for COD, nitrogen, and phosphorous content. Nutrient nitrogen and phosphorus should be present in the following ratio: COD/N/P = 200/5/1. Nutrient deficient feed samples will be supplemented with appropriate additions of ammonium hydroxide and sodium phosphate. When the first BOD results are obtained, nutrient addition will be modified, if necessary, to the following: BOD/N/P = 100/5/1.

After the 15th day of the acclimation period, the reactor should be ready for the CAD screening procedure for biological oxidation. If the schedule does not permit screening to be performed on the 16th day, the reactor should be fed daily at the 15th day feed rate, until the CAD test composite sample is available.

COD, specified above as the principal monitoring analyses, should be replaced with a TOC analysis as soon as the CAD mobile test facility (with its TOC analyzer) is on the site.

2.4.3.7 Procedure--

The test composite sample will at this time have already passed through both the byproduct removal steps and treatment for solids removal. The volume required for biological oxidation (BIO) and air stripping/oxidation (ASO) testing is 300 liters (150 liters for each). The remainder of the composite sample will be held for the Carbon-1 treatment step (Section 2.4.2).

Perform a TOC analysis on the 300-liter composite and add the required nutrients as described in Section 2.4.3.6. Check the pH of the sample and adjust to between 6.0 and 8.0 with H_2SO_4 or NaOH, if necessary.

Stop the air flow to the reactor being used for seed acclimation, evaporative losses, and allow the solids to settle. Syphon off the supernatant, measure its TOC, and discard.

Prepare a second reactor for comparison air stripping/oxidation. The volume of sludge remaining in the biological unit after syphoning should be measured and an identical volume of water will be added to the ASO unit to approximate the dilution factor encountered in the BIO unit. Add 150 liters of sample to each reactor and begin aeration.

Adjust the air flow in the BIO system to provide good solids mixing. The ASO unit should receive the same amount of air flow as measured by the rotameters. Aerate both systems for 48 hours. Dissolved oxygen, oxygen uptake rate and pH should be checked periodically on the BIO unit. The dissolved oxygen available in the system should be at least 2 mg/l. The pH of the system should be maintained at between 6 and 8.

At the end of the aeration period, stop the air flow to both units, adjust for evaporation, and syphon 150 liters from each unit after the solids in the BIO unit have settled. Submit 10 liters (25 liters if modified bioassy testing is desired) of each sample for Level 1 analyses. The biologically treated sample will be used for Carbon-2 screening. (Section 2.4.2)

2.4.4 Ion Exchange

2.4.4.1 Introduction--

The ion exchange process is used to remove inorganic ions from water. Standard practice is to first remove turbidity and organics from the waste stream by other means, then introduce the water into a column filled with an ion exchange resin. Ions in the waste stream are replaced by ions provided by the ion exchange media, by means of a substitution reaction. Different types of resins are available depending on the ion or groups of ions to be removed. Naturally occurring substances which display ion exchange properties include greensand (glauconite) and bentonitic clay. The development of synthetic organic resins has made it possible to produce materials with varying ion exchange properties, capable of removing a wide range of cationic and anionic materials. The four basic types of ion exchange media include strong acid, weak acid, strong base and weak base.

2.4.4.2 Summary of Method--

The wastewater sample is passed through a series of three columns containing appropriate ion exchange resins for removal of toxic metals.

2.4.4.3 Apparatus--

Three 3-inch I.D. glass columns - 45-inches in length, fitted with a 50-mesh support screen and bottom drain valve.

1 - Variable speed pump with teflon tubing

2 - Sample storage and collection vessels - capacity 25 gal. each.

Filtration equipment as described in Section 2.4.1.

2.4.4.4 Reagents--

Deionized water

Strong Acid type ion exchange resin
  (Rohm & Haas Amberlite IR-120 plus-Sodium form or equivalent).

Weak Acid type ion exchange resin
  (Amberlite DP-1 or equivalent).

Strong Base type ion exchange resin
  (Amberlite IRA-402 chloride form or equivalent).

2.4.4.5 Preparation--

Introducing a non-filtered feed to the resins may result in a build-up of suspended particles at the top of the resin bed causing channeling of the influent stream or excessive pressure drop. To avoid this possibility, the composite sample will be filtered according to the procedures described in Section 2.4.1 before ion exchange screening is begun.

2.4.4.6 Procedure--

A. Charging the columns.

NOTE: Always fully hydrate the resin according to the manufacturer's instructions before charging it to a column, and make sure the column already contains some water during charging. Never allow a charged column to become dry, since hydration may cause enough expansion of the resin to break the glass column.

1. Add a slurry of the strong acid resin to the first column until a depth of 30 inches is reached. During the addition of the slurry, occasional draining of the excess water will be required to prevent overflowing the column. However, do not allow the liquid to fall below the resin level. Measure and record the amount of water added with the slurry and drained from the columns for use in calculating the dilution factor.
2. Repeat step A with the weak acid resin (column 2 in series) and the strong base resin (column 3), adding each resin to a depth of 30 inches.

B. Backwashing the columns

1. Attach the pump line to the bottom of the column.
2. Slowly start the flow of deionized water up through the column.
3. Increase the flow rate until all air pockets are removed and all resin particles have achieved mobility. The proper flow rate should produce a 50% expansion of the bed. Any extremely small particles may be allowed to pass out of the column.
4. After ten minutes of backwashing, stop the flow and let the resin settle by gravity.
5. Drain the excess water to a level of approximately 0.5 inch above the resin level.
6. Repeat steps 1 through 5 for columns 2 and 3.

D. Adsorption

1. Pump the filtered sample to the first column (strong acid) at a rate of approximately 200 ml/min.

2. Adjust the stopcock at the bottom of the column so that a constant liquid level is maintained above the resin. Collect the effluent from the first column and begin feeding to the second column at the same rate. Continue this process through the third column.
3. After the sample has passed through all three resin columns, measure the amount of sample collected and submit 10 liters of the sample for Level 1 analysis. Record the amount of deionized water initially added to the columns for use in calculating the dilution factor.

2.4.5 Chemical Oxidation

2.4.5.1 Introduction

Phenolic compounds and numerous other organic chemicals can be destroyed by reaction with an oxidizing agent. The choice of an oxidizing agent rests primarily on its rate of reaction, selectivity, cost and ease of handling. Several chemical oxidants which are commonly used include:

1) Ozone and oxygen,
2) Hydrogen peroxide,
3) Potassium permanganate, and
4) Chlorine and chlorine containing compounds.

For thermodynamically reversible reactions, the oxidation-reduction potentials can be used as a quantitative measure of "oxidizing power," however, most reactions involving oxidation of organic chemicals are irreversible, and therefore, the redox potentials are of little use for predicting expected behavior.

2.4.5.2 Summary of Method

Hydrogen peroxide will be added to the composite sample to oxidize any remaining organic components.

2.4.5.3 Apparatus

Container for composite sample,
Stirring apparatus (Lightning mixer or equivalent),
Portable dissolved oxygen meter.

2.4.5.4 Reagents

Hydrogen peroxide - 50%

2.4.5.5 Procedure

Measure the dissolved oxygen concentration in the sample remaining after ion exchange treatment. Cautiously add 50 ml of 50% hydrogen peroxide with mixing (toxic gases may evolve from this reaction). Repeat this procedure until a residual dissolved oxygen reading of at least 5 mg/l is maintained. Record the amount of hydrogen peroxide required and submit a 10-liter portion of the oxidized sample for Level 1 analysis.

SECTION 3

GASEOUS EMISSION METHODOLOGY

3.1 BACKGROUND

Control technology for screening of gaseous samples to determine potential treatment methods must include unit operations for the removal of particulates and gases/vapors of concern. Either class of materials may be organic or inorganic. The types of control technology for gas treatment include mechanical collection, electrostatic precipitators, filters, liquid scrubbers/contactors, condensers, solid sorbents and incineration.

Sampling and testing of gaseous streams for CAD is much more difficult than the relatively simple procedures specified for liquids. The inability to bring sufficient feed volume into the CAD mobile test facility (as is possible with liquid samples) limits the use of a number of unit operations and/or desirable strategies that can be applied in the gaseous emission screening methodology. The practicality of performing certain types or large numbers of CAD tests at the source may be restricted by such factors as limited working space on a platform, logistical problems servicing a platform, plant restrictions on use of non-explosion proof equipment, personnel safety, requirements for specialized equipment, and the analytical load generated by a broad test plan.

Based upon the above considerations, the CAD methodology for gaseous emissions was developed to be flexible but more reliant on process information. This permits the user of CAD to be selective in choosing a screening system and may allow a more simplified approach to certain streams. The screening test sequences are presented in Figure 5.

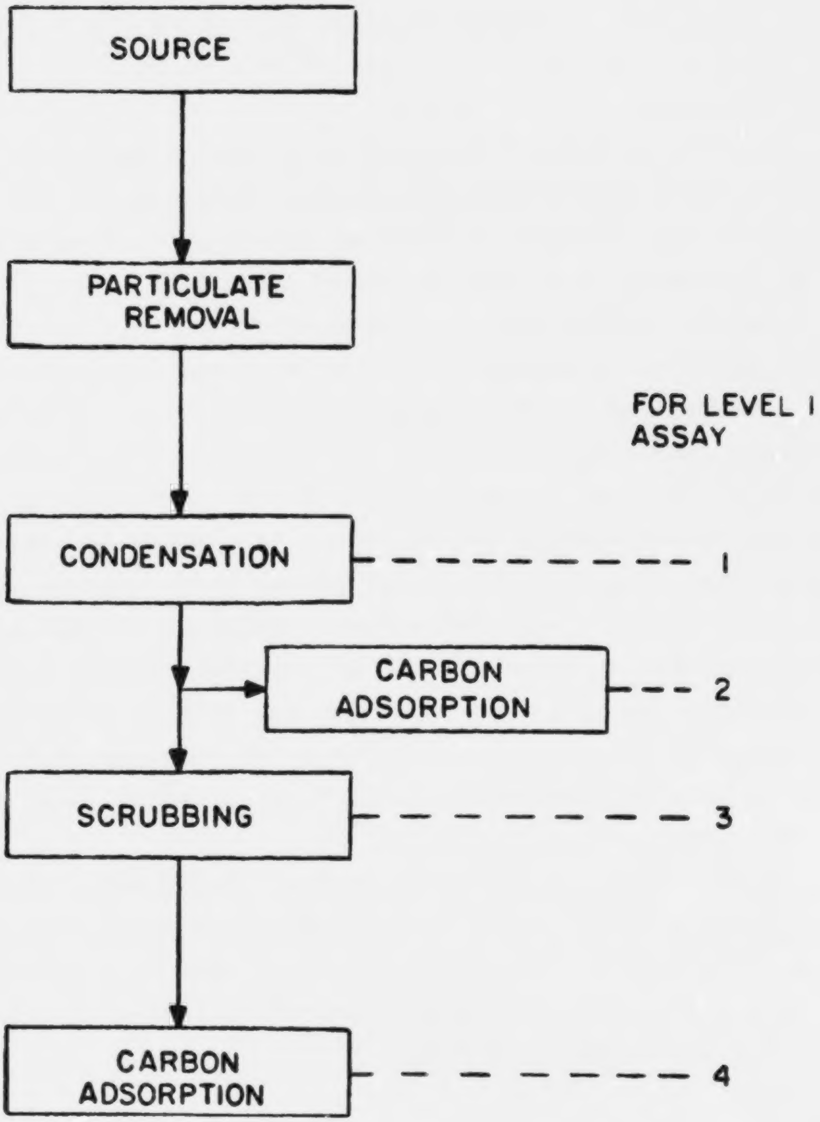

SOURCE
PARTICULATE REMOVAL
FOR LEVEL I ASSAY
CONDENSATION
1
CARBON ADSORPTION
2
SCRUBBING
3
CARBON ADSORPTION
4

Figure 5. Gaseous emission screening sequence.

3.1.1 Module Description

The control technologies recommended for gaseous emission screening methodology are:

1) Particulate removal,
2) Gas cooling (condensation),
3) Liquid scrubbing, and
4) Carbon adsorption.

The equipment for these operations is constructed and assembled as modules, and several combinations or sequences can be arranged. Details of the module arrangement (screening trains) are discussed in Sections 3.3, 3.4 and 3.5. Following is a brief description of each module and its function in CAD:

Particulate Removal--The module is a standard Source Assessment Sampling System (SASS) train cyclone/filter assembly, contained in a heated oven. For CAD screening purposes, this module serves only to pre-treat the gas when particulate is present.

Gas Cooling--Hot gases must be cooled to at least 130°F before entering an activated carbon module. In commercial practice, gases are often cooled to permit use of cheaper materials of construction (e.g., plastics) in downstream ducts and equipment. In addition to cooling as a protective measure, condensation of volatile material is a valuable control technology. This module also will be a standard SASS train component, except that the sorbent cartridge is not used and will be taken out of line.

Scrubbing--Liquid scrubbing, using an aqueous alkaline solution, is specified as the primary control technology in CAD screening for removal of pollutants in acid gases. Several media were investigated and sodium carbonate was selected. Carbon dioxide, a common component in many gaseous streams, will be absorbed in media such as sodium hydroxide, requiring a large volume of solution and causing logistical problems. The capacity to remove acidic components at expected concentrations cannot be handled in the standard SASS impinger assembly, therefore a small counter-current scrubber must be used.

Carbon Adsorption--Activated carbon is being studied for removal of trace quantities of organic and inorganic materials. The economics of regeneration usually preclude carbon being used as the primary technology for removal of high concentrations of organics. Regeneration will not be studied in CAD. The module is a column canister sized to contain a sufficient quantity of activated carbon. Calculations show that the capacity of a standard SASS sorbent module is not adequate for CAD studies.

3.1.1.1 Unit Operations Not Included--Unit operations considered for the gaseous emission methodology, but not included in the test sequence are: electrostatic precipitation, flaring, and incineration. Reasons for their exclusion are discussed below:

Electrostatic Precipitation--The selection of electrostatic precipitation technology depends heavily on conductivity and resistivity properties of the gas stream. Instead of testing a prototype electrostatic precipitator unit as a CAD screening procedure, measurement of these properties is recommended to supplement existing Level 1 protocols. They include:

1) Particle resistivity,
2) Particle size - average diameter,
3) Specific gravity,
4) Bulk density, and
5) Particle size distribution curve.

Direct Combustion (flare)--Flaring is acceptable control technology for a number of applications, principally in the petroleum refining and other industries where upset conditions involving large volumes of flammable gases can be economically handled. It is not recognized or recommended as best available control technology by regulatory agencies due primarily to lack of a sufficient data base. A major disadvantage is the absence of equipment and practical techniques to sample the products of combustion and monitor performance. Methods and equipment sizes used in pilot plant test runs are not practical for CAD and have not yielded data that can be used for scaled-up design or prediction of performance. The disadvantages of flares are presently too great for the unit operation to be useful in CAD.

Direct Flame Incineration--Thermal incineration is one of the most effective means for disposal of hazardous waste gases, and despite high capital and operating cost, will likely be specified more frequently in the future for problem pollutants. A proper evaluation of the capability of incineration would involve study of key parameters such as residence time and temperature.

The manipulation of a number of variables is beyond the scope of CAD and, coupled with the general difficulty of handling large volumes of sample, screening tests on incineration become impractical and are not recommended. Incinerator manufacturers, however, have compiled a large data base on the thermal oxidation of organic materials and there is also a high level of confidence that any organic material can be destroyed.

3.1.2 Applicability

The CAD gaseous emission screening methodology is applicable to any point source where a Level 1 environmental assessment might be performed. This is generally intended to mean those sources that discharge directly to the atmosphere, and does not normally include process lines, internal recycle or waste gas lines directed to control devices.

Open vents or stacks that are considered sources of uncontrolled fugitive emissions are not recommended for CAD. Examples of these sources include relief systems, pressure let-down or control systems, emergency vents, leaks, spills, etc. They are normally highly variable in composition, rate, frequency and duration, and control technology is often difficult or uneconomical to apply. When the materials are hazardous, it is common to collect the vapors in an exhaust system and direct the combined flow into a central control system such as a scrubber. Discharges from control systems are usually of interest to CAD.

3.1.2.1 Need for Process Review

Vents, stacks and other point sources of air emissions are usually too numerous in the plant site to permit a CAD assessment of each discharge. A cost effective program can best be achieved by performing a reasonably complete engineering review of the available data before finalizing sample points. Process and engineering flow sheets, process and treatment descriptions and all other information should be studied prior to a preliminary site visit. During the visit, information gaps may be filled by discussions with plant personnel and/or inspection of equipment and devices. If it can be established, for example, that the emission is a vapor and contains no particulate matter, the most complex and costly test configuration requiring particulate sampling modules can be avoided. Furthermore, if the source is a pure, single component organic material (such as breathing and filling vapors from a storage tank) CAD may not be needed at all because emissions can be calculated and potential control technology selected based on the material properties.

3.1.3 Sampling

IERL Level 1 sampling protocols are employed in CAD gaseous emission methodology. The sampling apparatus for a Level 1 assessment are the grab bulb for gaseous samples only, and the equipment package for gaseous streams containing particulate.

The general principles of IERL sampling apply to CAD, but may be modified to accommodate a more flexible approach in air methodology. This is best illustrated in Figure 6 which outlines alternative screening arrangements and associated sampling requirements. For CAD purposes, the standard SASS modules are used in the following manner:

1. The particulate removal module (cyclones and filter) is used only for the baseline sample, which will be collected and analyzed in strict accordance with Level 1 procedures for environmental assessment. The CAD screening train uses the same particulate removal module for preconditioning of the stream prior to entering control devices.
2. The gas cooling module of the SASS train is used in CAD for evaluating condensation control technology. Operating this module according to Level 1 assessment parameters will serve both as condensation screening technology and the means to provide a sample for evaluation of the applicability and effectiveness of condensation.
3. The XAD-2 cartridge and the impinger module in the sampling system is designed to collect the residual pollutants. A side benefit is the removal of corrosive material which would cause damage to the vacuum pump, dry gas meter and other components downstream.

The complete Level 1 analytical protocols shall be performed on the gas samples produced. The CAD sample sizes shall meet the requirements of these protocols which presently are:

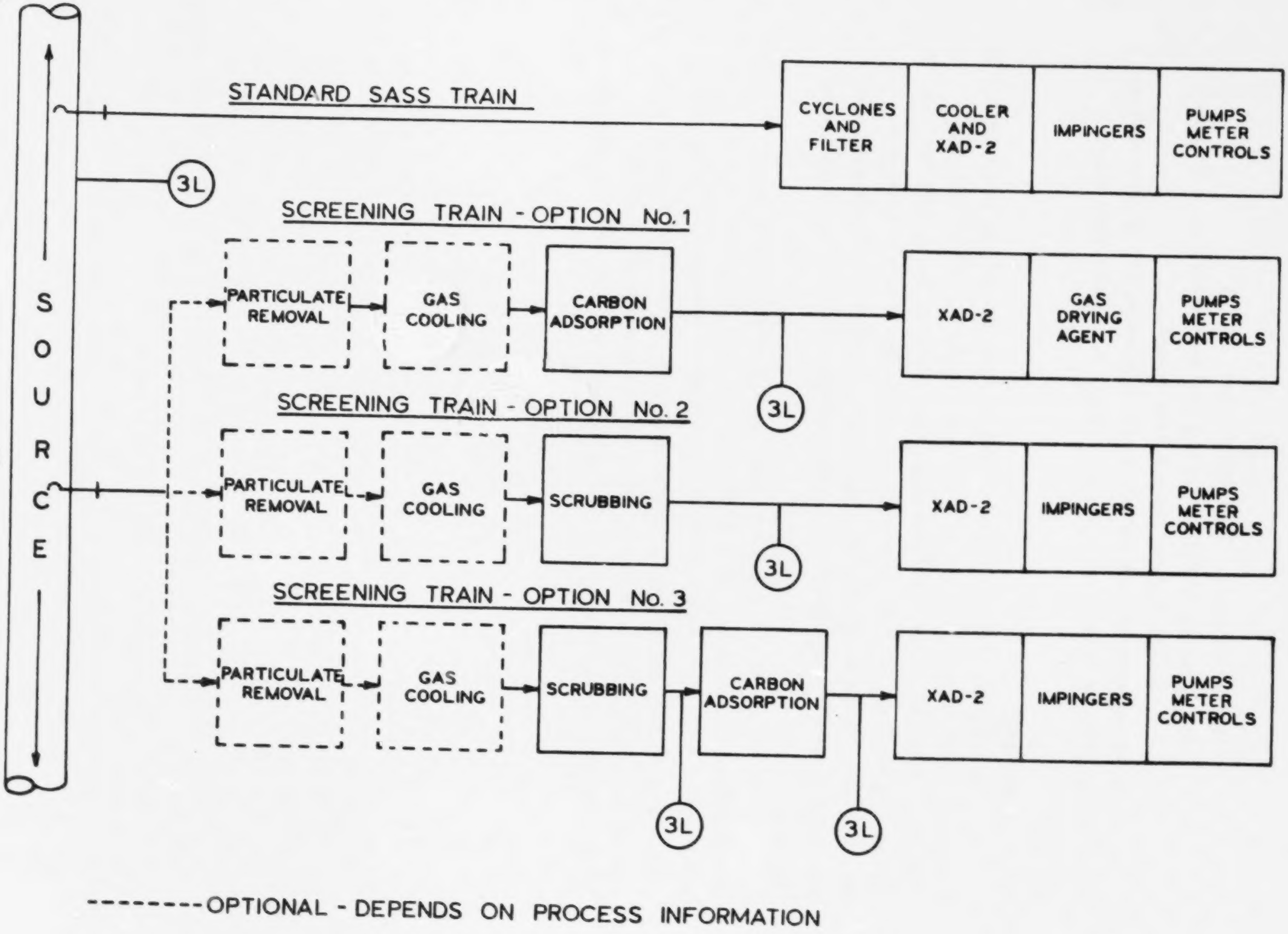

S O U R C E
STANDARD SASS TRAIN
CYCLONES AND FILTER
COOLER AND XAD-2
IMPINGERS
PUMPS METER CONTROLS
3L
SCREENING TRAIN - OPTION No. 1
PARTICULATE REMOVAL
GAS COOLING
CARBON ADSORPTION
XAD-2
GAS DRYING AGENT
PUMPS METER CONTROLS
3L
SCREENING TRAIN - OPTION No. 2
PARTICULATE REMOVAL
GAS COOLING
SCRUBBING
XAD-2
IMPINGERS
PUMPS METER CONTROLS
3L
SCREENING TRAIN - OPTION No. 3
PARTICULATE REMOVAL
GAS COOLING
SCRUBBING
CARBON ADSORPTION
XAD-2
IMPINGERS
PUMPS METER CONTROLS
3L
3L
--------OPTIONAL - DEPENDS ON PROCESS INFORMATION

Figure 6. Gaseous emission screening train alternatives

1) GC analysis: 3 liters (grab);
2) Physical/chemical testing and health effects: 30 cubic meters (passed through SASS train).

It is recommended that all personnel performing CAD gaseous emission screening be familiar with Level 1 S/A protocols, especially SASS train operation.

3.1.4 Analysis

In order to obtain meaningful results from the tests, it is imperative that each source to be evaluated be sampled according to the Level 1 IERL methods in addition to the screening sampling. Ideally, both tests will be run simultaneously. If this is not possible, process data for each source must be evaluated to determine the constancy of operation and judgement must be used to assess the reliability of comparing data from two non-simultaneous test runs.

The scope of CAD field work may require certain handling, preparation and preservation procedures and limited analyses on samples that must be performed on site for reasons of impracticability of shipment, deterioration within a short time period, etc. Additionally, specific tests necessary for CAD characterization data to assist in field decisions would be needed. Level 1 physical, chemical and bioassay procedures are described in Reference 2.

3.2 PRELIMINARY MEASUREMENTS

3.2.1 Introduction

Preparing the site so that equipment can be positioned properly is frequently the most difficult and time consuming part of sampling. All sites should be inspected prior to sampling to determine the best probe locations, scaffolding requirements, availability of electrical connections at the sampling site, restricted areas and safety hazards. Flow rates through the SASS train and the screening train(s) will be "pseudo-isokinetic" as prescribed for Level 1 assessment sampling. Several parameters must be measured before screening tests can be performed. These parameters include stack geometry, gas temperature, velocity and moisture content.

Before any screening tests can be performed, all preliminary measurements must be made, and the site prepared for sampling. Process data will be acquired previous to a sampling run to determine which screening trains will be used.

3.2.2 Apparatus

Tape measure

Temperature gauge (Thermocouple, or equivalent, to measure stack temperature to within 1.5 percent of the minumum absolute stack temperature).

Pitot tube (Type S with a coefficient within ± 5 percent over the working range).

Differential pressure gauge (Inclined manometer, to measure velocity head to within ± 10 percent of the minimum value).

Barometer (To measure atmospheric pressure to within 0.1 inch Hg).

Probe* (Stainless steel or glass sufficiently heated to prevent condensation, with glass wool plug to remove particulate matter).

Impingers* (Two midget impingers - 30 ml capacity).

Ice bath container* (To condense moisture in impingers).

Silica gel tube* (To protect pump and dry gas meter).

Pump* (Leak-free, diaphragm type, or equivalent).

Dry gas meter (To measure within 1 percent of total sample volume).

Graduated cylinder (25 ml).

Balance - Triple beam.

Wet bulb dry-bulb apparatus.

Orsat apparatus.

---

*Optional - needed only if condenser method for moisture determination is used.

3.2.3 Reagents

Distilled water

Silica Gel (Indicating type)

Orsat solutions

3.2.4 Stack Geometry, Temperature and Gas Velocity Measurements

a. Select the sampling site and number of traverse points required according to accepted procedures, as shown in Reference 3. Circular stacks will require two sample ports located 90 degrees apart. The number of sample ports for rectangular stacks is determined by the cross-sectional area (equivalent diameter) and flow characteristics. It is preferable to locate the sample ports on a vertical run whenever possible. When the flues are under a negative draft, standard 3-inch couplings with caps are sufficient.

b. Measure the inside diameter of the stack. For rectangular stacks, use the following equation to calculate the equivalent diameter:

$$\text{Equivalent Diameter} = \frac{2\ (\text{length x width})}{\text{length} + \text{width}}$$

c. Perform a standard velocity traverse and measure the absolute pressure in the stack. A thermocouple should be attached to the tip of the pitot tube during the traverse. Record the temperature and velocity head at each traverse point.

d. Calculate the average velocity head and temperature of the stack and record these values. These data will be used later to calculate the sampling flow rate according to procedures given in Reference 4.

3.2.5 Moisture Content

3.2.5.1 Wet Bulb - Dry Bulb Method

Moisture content may be measured by the wet bulb-dry bulb method if the dry bulb temperature is below 212°F and it is expected that the percentage of moisture will be below 15 percent. A psychometric chart and instructions for use of the apparatus are included in the wet bulb-dry bulb sampling kit.

If it is obvious that the gas stream is saturated with moisture (presence of liquid droplets in the gas stream), use the average stack temperature calculated in Section 3.2.4, and the psychometric chart to determine the percent moisture.

3.2.5.2 Condenser Method

When the above methods cannot be used, the condenser method must be used. This procedure is detailed in Reference 3.

3.2.6 Gas Composition

Measure the stack gas composition using an Orsat analyzer.

3.3 SCREENING PROCEDURES WITH CARBON

3.3.1 Introduction

Any gas or vapor (adsorbate) will adhere to some degree to any solid surface (adsorbent) due to the van der Waals forces which are encountered on the surface of the solid. This phenomenon is known as physical adsorption. Sometimes an adsorbate will become chemically bonded to the adsorbent (chemisorption).

Adsorption (chemical and/or physical) as an air pollution control method is used as a means of concentrating objectionable or toxic substances, thus facilitating their disposal or recovery. True gases such as hydrogen, nitrogen, oxygen, carbon monoxide and methane are virtually nonadsorbable at ambient temperatures by physical means. Low-boiling vapors (B.P.-100° to 0°C) are moderately adsorbable and adsorption efficiency can be increased by refrigeration. Heavier vapors (B.P. 0°C) are readily adsorbed by activated carbon at ordinary temperatures. In general, the higher the molecular weight and/or critical temperature, the greater the weight capacity and preference. Aromatic and/or non-polar gases are preferentially adsorbed. At 50 percent humidity or lower, water vapor present in a gas stream generally will not affect adsorption capacities for other materials and will provide some cooling of the carbon bed.

Activated carbon is used in CAD for removal of low concentrations (1%) of organic and inorganic pollutants. High concentrations would rapidly overload the carbon dose used in screening. In commercial practice, carbon is not normally used for removal of high concentrations of pollutants because of the higher costs of large carbon systems and regeneration equipment.

Condensation is a potential technology to reduce organic loading, and this option can be conveniently added to the screening system. Gas cooling also becomes necessary to protect the carbon from high temperatures and concomitantly, to reduce desorption. When needed, the gas cooling module can be standard SASS equipment.

Particulate, when present, should be removed to prevent plugging of the carbon bed. Tars, oils and gummy material, in particular, will coat the carbon and reduce the available surface area. The standard SASS cyclone and filter section may be used as the particulate removal module.

3.3.2 Summary of Method

Stack gases are passed through a heated probe to a series of heated cyclones and a final filter, all housed in a $400^{\circ}F$ oven, for removal of particulate matter when required. Next, the gases are cooled by passing through a water-cooled condenser. The gas stream, at a temperature of $130^{\circ}F$ or less, is passed through a canister filled with activated carbon. The treated stream is then pulled through a modified SASS train which will collect all components not removed by activated carbon.

3.3.3 Apparatus

The list of apparatus needed for gaseous emission screening with the carbon column is given below:

1. Standard SASS train;
2. Grab sampling bulb - 3 liter capacity, fitted with a stopcock valve and sample probe (Figure 7);
3. A canister - To contain 4.5 kg of activated carbon; 6-inch diameter cylinder 24 inches in length, and
4. Grab sampling bulb - 3 liter capacity, fitted with two stopcock valves (Figure 9).

Note: The pumps, probes, gas meters, temperature and pressure gauges, etc., which are available in a Standard SASS train, will be utilized during the screening tests.

3.3.4 Reagents

1. Silica gel - Indicating type, 3 to 8 mesh (2 kg)
2. XAD-2 - Sorbent resin (500 gms)
3. 30 percent solution H_2O_2 - (1 liter)
4. 0.02M silver nitrate - (1 liter)
5. 0.02M ammonium persulfate - (1 liter)
6. Activated carbon - Calgon type BPL or equivalent - (5 kg)

3.3.5 Preparation

See Section 3.2 before proceeding with screening train preparation.

Figure 8 shows the configuration of the train to be used for carbon evaluation. Assemble the components of the train as shown. Detailed instructions for set-up of standard SASS train items are included in Reference 4.

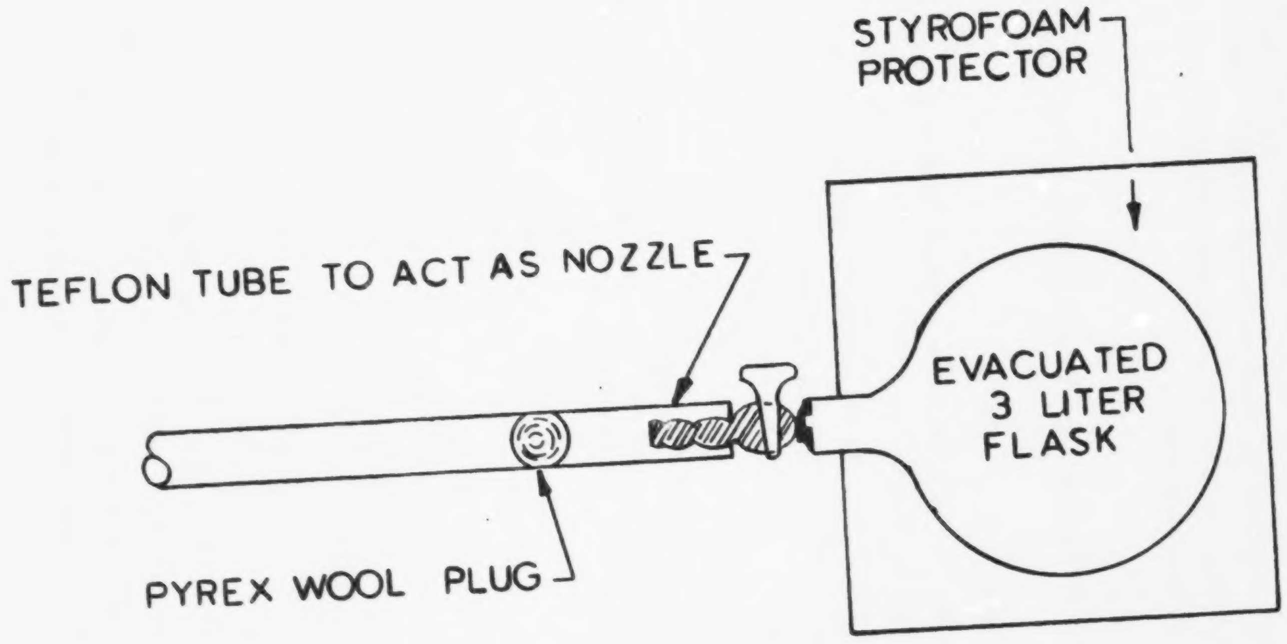

STYROFOAM PROTECTOR
TEFLON TUBE TO ACT AS NOZZLE
EVACUATED 3 LITER FLASK
PYREX WOOL PLUG

Figure 7. Grab sampling bulb.

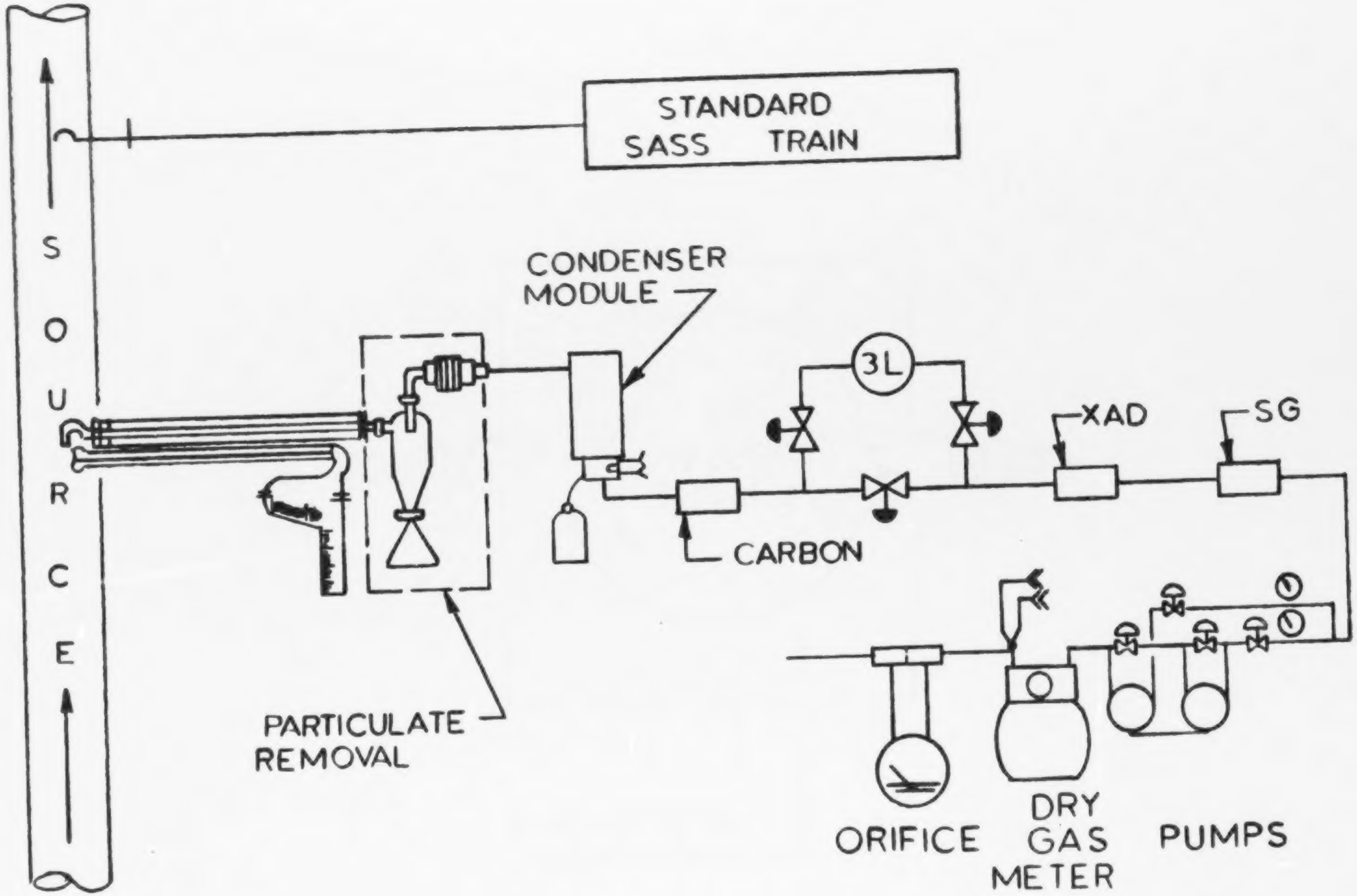

STANDARD
SASS TRAIN
CONDENSER
MODULE
3L
XAD
SG
CARBON
S
O
U
R
C
E
PARTICULATE
REMOVAL
ORIFICE
DRY
GAS
METER
PUMPS

Figure 8. Carbon screening train.

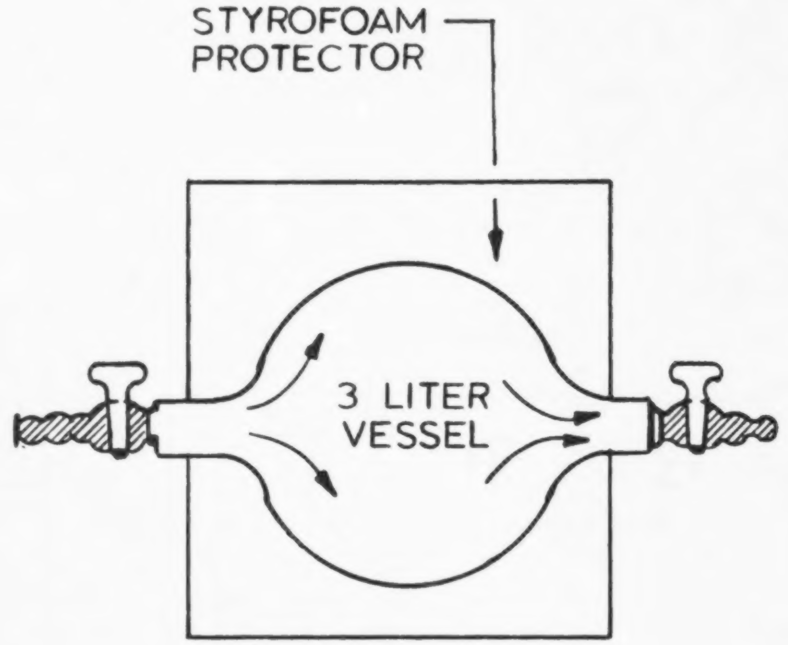

STYROFOAM
PROTECTOR
3 LITER
VESSEL

Figure 9. Grab sampling bulb with dual stopcock arrangement.

The following steps are necessary to prepare the train for sampling:

1. Place a filter in the filter holder;
2. Place approximately 5 kg of activated carbon into the carbon canister and seal;
3. Place 130 gms of XAD-2 and 500 gms of silica gel in their respective canisters and seal;
4. Perform the standard leak test as required by Level 1 protocol, and replace or repair any components which do not meet leak testing requirements; and
5. Transport the equipment to the test site.

Arrangements should be made at this time for gathering of process operation data during the sampling period. Be sure that an adequate supply of ice is available (each train may require as much as 100 lbs/hr during the sampling period). Using the preliminary data obtained in section 3.2 of this procedure, calculate the required sampling nozzle size and sample flow rate, as shown in Reference 4. Attach the nozzle to the probe and perform a leak test to assure that the equipment was not damaged during transportation to the site. Energize all components which require heating/cooling, i.e. probe, cyclone oven, gas cooling device. When these components have attained the designated temperatures, proceed to section 3.3.6.

3.3.6 Sampling Procedure

Place the probe in the stack and position the nozzle at the point of average velocity. Record all necessary train operation data (gas meter reading, temperatures, stack gas flow rate). Start the pumps and set the sampling flow rate to the proper value as calculated from the average velocity data and nozzle size. Operate the train until a minimum of 1000 cubic feet of gas has been sampled, as indicated by the gas meter. If particulate build-up causes a severe increase in vacuum and corresponding drop in sample flow rate, the test must be halted to replace the filter. Monitor the temperatures through the condensate trap and the impinger train. The gas temperature leaving the condensate trap should not be allowed to exceed 130°F. Condensate will build up in the trap and must be transferred periodically to the condensate collection bottle. The detailed procedure is given in Reference 4.

Toward the end of the sample run (900 to 1,000 ft^3 sampled) a 3-liter grab sample will be taken for GC analysis. This is accomplished by placing a 3-liter sampling bulb in line and momentarily diverting the gas flow through the bulb (Refer to Figure 9). Open valves 2 and 3 and then close valve number 1. Leave the valves in this position for one minute to ensure proper flushing of the sample container. After the sample has been taken, open valve 1 and close valves 2 and 3. Remove the bulb from the line and transport to the van for GC analysis. Level 1 procedures are used to analyze for low-molecular weight hydrocarbons in this sample.

When sufficient sample volume has been collected by the train, shut down the pumps by first closing the coarse control valves. When the vacuum gauge has dropped to zero, the pump switches may be turned off. Record the final gas meter reading and all temperature readings.

3.3.7 Sample Handling Procedures

Remove the probe from the stack and turn off all heating/cooling elements. Opening the oven door will speed cooling of the oven and contents. Remove the XAD-2 cartridge, seal the ends, tag the sample and submit for Level 1 analysis. Remove the cyclone and filter assembly, discard the collected particulate matter and clean all surfaces. Remove the silica gel from its canister and clean the container. Transfer the condensate sample to a separatory funnel. Using a pH meter, adjust the pH to 7.0 with ammonium hydroxide or hydrochloric acid. Extract the sample with three 50-ml portions of methylene chloride. Tag this sample and submit as "Organic Extract." Divide the remaining aqueous sample into two equal parts. Using a pH meter, adjust each part as follows:

Part A - Acidify to pH less than 2 with nitric acid.

Part B - Adjust pH to 12 with sodium hydroxide.

Transfer each part to a suitable size polyethylene bottle for shipment to the home laboratory.

Empty the carbon canister and discard the spent carbon.

3.4 GAS SCREENING PROCEDURES WITH SCRUBBING MODULE

3.4.1 Introduction

Wet scrubbing is a term used to broadly describe vapor-liquid mass transfer operations. In scrubbing, one or more components are removed from the gas phase by absorption into the liquid phase. Absorption depends on a solubility mechanism but may be followed by chemical reaction once in solution. Absorption is enhanced by high diffusion rates, high solubilities, large interfacial areas and turbulence. Numerous equipment designs are commercially available which promote contact of the vapor and liquid.

Scrubbing methodology for gaseous emission CAD is designed primarily for the removal of acidic pollutants in the gas stream. Some organic components will also be absorbed. Among the aqueous alkaline scrubbing media investigated were caustic soda, lime, carbonate, magnesia and ammonia. Organic sorbents were not considered because they are generally operated under high pressure and/or low temperature. Sodium carbonate was selected as a broad base sorbent with the advantage of being insensitive to high concentrations of CO_2. Carbon dioxide is a major component in many sources of possible interest to CAD. Design for CO_2 removal, in addition to other priority pollutants, would result in excessively large equipment and solution requirements.

The scrubber module is a packed column, 4-inch dia. and 5-ft long, containing a 3-ft depth of 1/2-inch Raschig rings. Scrubbing solution (2-M sodium carbonate - 16 liters) will be recirculated through the packed column until the pH drops to 10.0, when the test will be stopped to replace the spent solution.

Preceding the scrubber module are gas cooling and particulate removal modules. These were described in Sections 3.1 and 3.3.

The sampling portion of the overall train contains the SASS sorbent module (XAD-2), for collection of organic components not removed in screening, and the SASS impinger module for collection of inorganic components.

3.4.2 Summary of Method

Stack gases are passed through a series of cyclones and final filter, all housed in a heated 400°F oven. The gas is then cooled to 130°F in a water-cooled condenser. Gases next pass through a scrubber module consisting of a packed tower utilizing a counter-current flow of alkaline solution. Leaving the screening section of the train, the treated gas enters the sampling section where standard SASS modules will collect any remaining pollutants.

3.4.3 Apparatus

For a list of apparatus needed for gaseous emission screening with the scrubber column, refer to Section 3.3.3. Delete item 3, (the carbon canister) and add the following:

1. Scrubber column - 4-inch diameter by 5 feet in length, packed with 1/2-inch Raschig rings (3 feet of packing); and equipped with a 16-liter reservoir and recirculation pump (See figure 10); and
2. pH meter and probe.

3.4.4 Reagents

For a list of reagents needed for gaseous emission screening with the scrubber column, refer to Section 3.3.4. Delete item 6 (activated carbon), and add the following:

1. 2-M sodium carbonate - (16 liters). Make an additional batch (16 liters) for replacement solution; and
2. Fiberglass filters - (142 mm x 0.016 inch).

3.4.5 Preparation

See Section 3.2 before proceeding with screening train preparation.

Figure 11 depicts the configuration of the train to be used for scrubber evaluation. Assemble the components of the train as shown. Detailed instructions for set-up of standard SASS train items are included in Reference 4. The following steps are necessary to prepare the train for sampling:

1. Place a filter in the filter holder;
2. Fill the scrubbing solution reservoir with sodium carbonate solution - approximately 16 liters;
3. Place 130 gms of XAD-2 resin in the appropriate canister and seal;
4. Fill the standard SASS impingers with appropriate reagents;

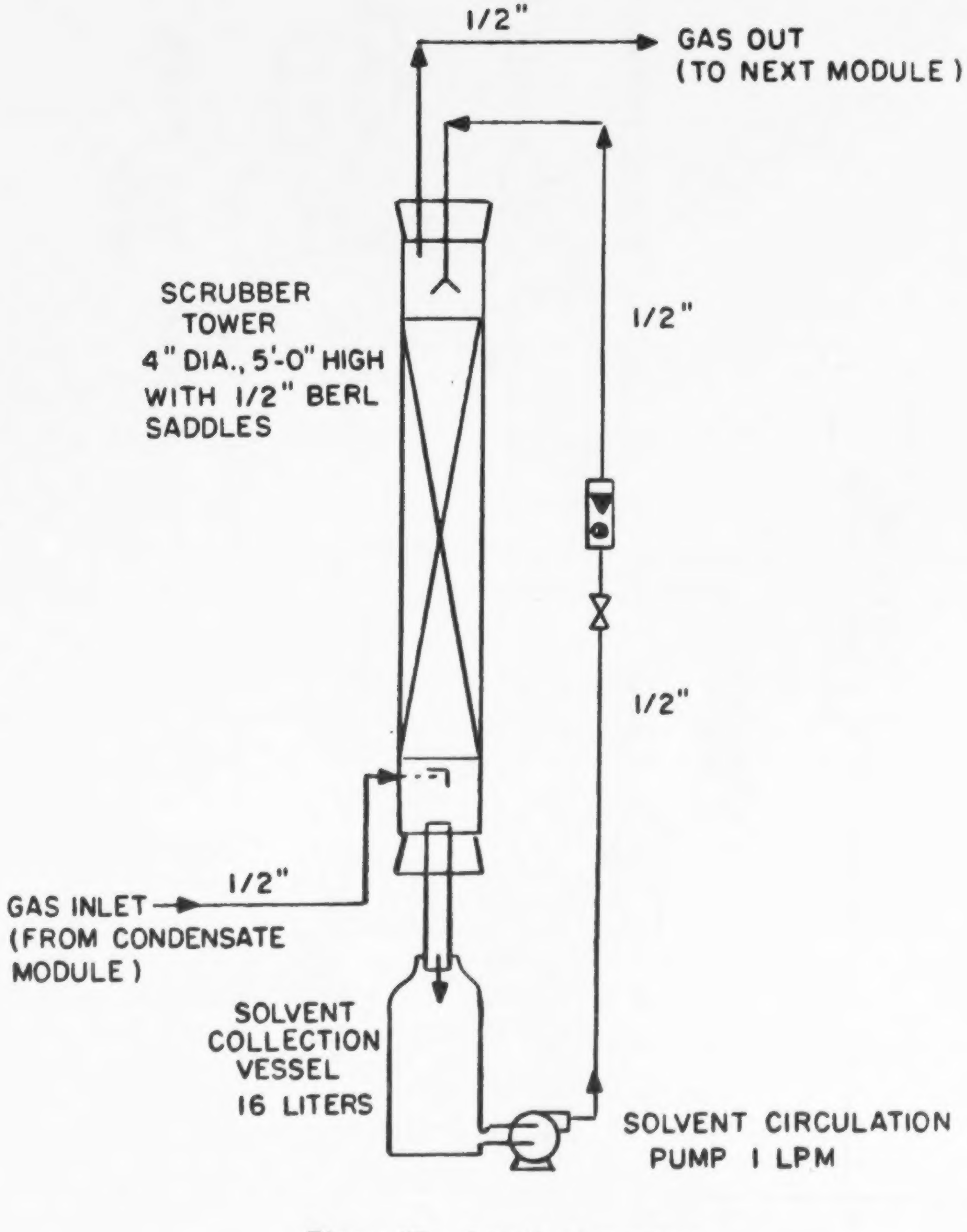

1/2"
GAS OUT
(TO NEXT MODULE)
SCRUBBER
TOWER
4" DIA., 5'-0" HIGH
WITH 1/2" BERL
SADDLES
1/2"
1/2"
GAS INLET
(FROM CONDENSATE
MODULE)
1/2"
SOLVENT
COLLECTION
VESSEL
16 LITERS
SOLVENT CIRCULATION
PUMP 1 LPM

Figure 10. Detail of scrubber.

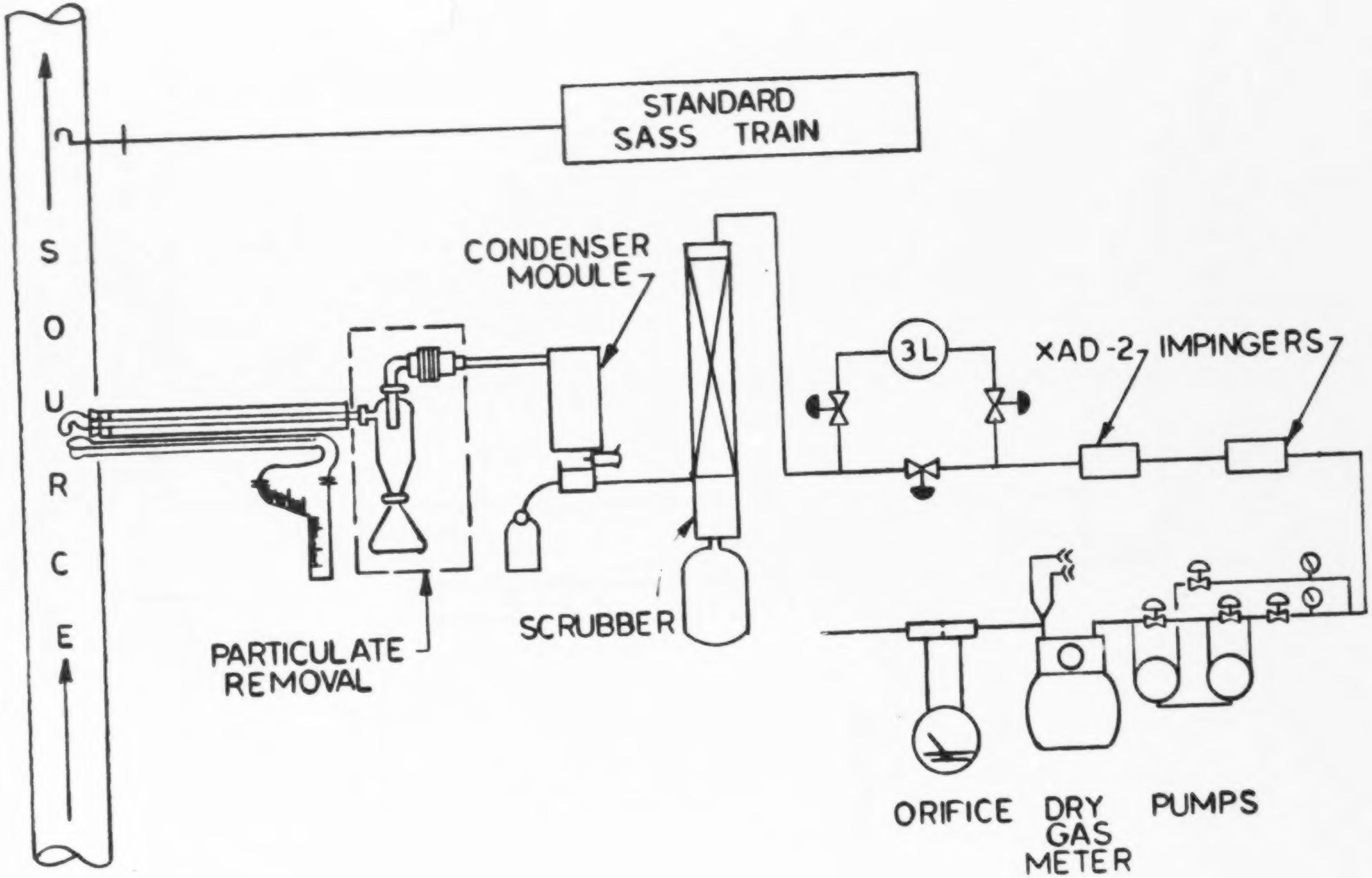

STANDARD SASS TRAIN
S O U R C E
CONDENSER MODULE
3L
XAD-2
IMPINGERS
SCRUBBER
PARTICULATE REMOVAL
ORIFICE
DRY GAS METER
PUMPS

Figure 11. Scrubber screening train

5. Perform the standard leak test as required by Level 1 protocol, and replace or repair any components which do not meet leak testing requirements; and
6. Transport the equipment to the test site.

Arrangements should be made at this time for gathering of process operation data during the sampling period. Be sure that an adequate supply of ice is available (each train may require as much as 100 lbs/hr during the sampling period). Using the preliminary data obtained in Section 3.2 of this procedure, calculate the required sampling nozzle size and sample flow rate, as shown in Reference 4. Attach the nozzle to the probe and perform a leak test to assure that the equipment was not damaged during transportation to the site. Turn on the scrubber solution recirculation pump and set the flow to approximately 1 liter/minute. Energize all components which require heating/ cooling, i.e., probe, cyclone oven, gas cooling device. When these components have attained the designated temperatures, proceed to Section 3.4.6.

3.4.6 Sampling Procedure

Place the probe in the stack and position the nozzle at the point of average velocity. Record all necessary train operation data (gas meter reading, temperatures, stack gas flow rate). Start the pumps and set the sampling flow rate to the proper value as calculated from the average velocity data and nozzle size. Operate the train until a minimum of 1,000 cubic feet of gas has been sampled, as indicated by the gas meter. If particulate build-up causes a severe increase in vacuum and corresponding drop in sample flow rate, the test must be halted to replace the filter. The scrubbing solution should also be replaced at this time. Monitor the temperatures through the condensate trap and the impinger train, and the pH of the scrubbing solution. A pH of less than ten is not acceptable and the scrubber solution should be replaced if the pH drops below ten. Condensate will build up in the trap and must be transferred periodically to the condensate collection bottle. The detailed procedure is shown in Reference 4.

Toward the end of the sample run (900 to 1,000 ft^3 sampled) a 3-liter grab sample will be taken for GC analysis. This is accomplished by placing a 3-liter sampling bulb in line and momentarily diverting the gas flow through the bulb (Refer to Figure 9). Open valves 2 and 3 and then close valve number 1. Leave the valves in this position for one minute to ensure proper flushing of the sample container. After the sample has been taken, open valve 1 and close valves 2 and 3. Remove the bulb from the line and transport to the van for GC analysis. Level 1 procedures are used to analyze for low-molecular weight hydrocarbons in this sample.

When sufficient sample volume has been collected by the train, shut down the pumps by first closing the coarse control valves. When the vacuum gauge has dropped to zero, the pump switches may be turned off. Record the final gas meter reading and all temperature readings.

3.4.7 Sample Handling Procedures

Remove the probe from the stack and turn off all heating/cooling elements. Opening the oven door will speed cooling of the oven and contents. Stop circulation of scrubbing solution. Remove the XAD-2 cartridge, seal the ends, tag the sample and submit for Level 1 analysis. Remove the cyclone and filter assembly, discard the collected particulate matter and clean all surfaces. Transfer the condensate sample to a separatory funnel. Using a pH meter, adjust the pH to 7.0 with ammonium hydroxide or hydrochloric acid. Extract the sample with three 50-ml portions of methylene chloride. Tag this sample and submit as "Organic Extract." Divide the remaining aqueous sample into two equal parts. Using a pH meter, adjust each part as follows:

Part A - Acidify to pH less than 2 with nitric acid.
Part B - Adjust pH to 12 with sodium hydroxide.

Transfer each part to a suitable size polyethylene bottle for shipment to the home laboratory.

The spent sodium carbonate solution may be discarded at this time.

Clean-up of the remainder of the train should follow procedures specified by Level 1.

3.5 GAS SCREENING PROCEDURES WITH SCRUBBING AND CARBON ADSORPTION MODULES

3.5.1 Introduction

Scrubbing and carbon adsorption are presented individually in Sections 3.3 and 3.4 as the basic control technologies for CAD gaseous emission methodology. When these two operations are run in series with particulate removal and condensation, the total screening system offers the most versatile CAD approach to a complex gas stream containing all classes of pollutants. If process knowledge of a source under investigation is inadequate to lead to the proper selection of a simpler system, the total train should be specified.

A complete set of Level 1 samples can be recovered from the total train configuration. Analyses of residual pollutants captured by the SASS sorbent and impinger modules will indicate the effectiveness of the combined screening operations for removal of pollutants. The individual effectiveness of the carbon or scrubber module can be determined by analyzing the grab samples taken before and after each module.

3.5.2 Summary of Method

Stack gases are passed through a series of screening operations and into a sampling section, as illustrated in Figure 12 and under conditions described in Sections 3.3.2 and 3.4.2.

3.5.3 Apparatus

The combined screening train utilizes all of the modules required for the scrubber and the carbon screening tests. The list of apparatus required as presented in Sections 3.3.3 and 3.4.3.

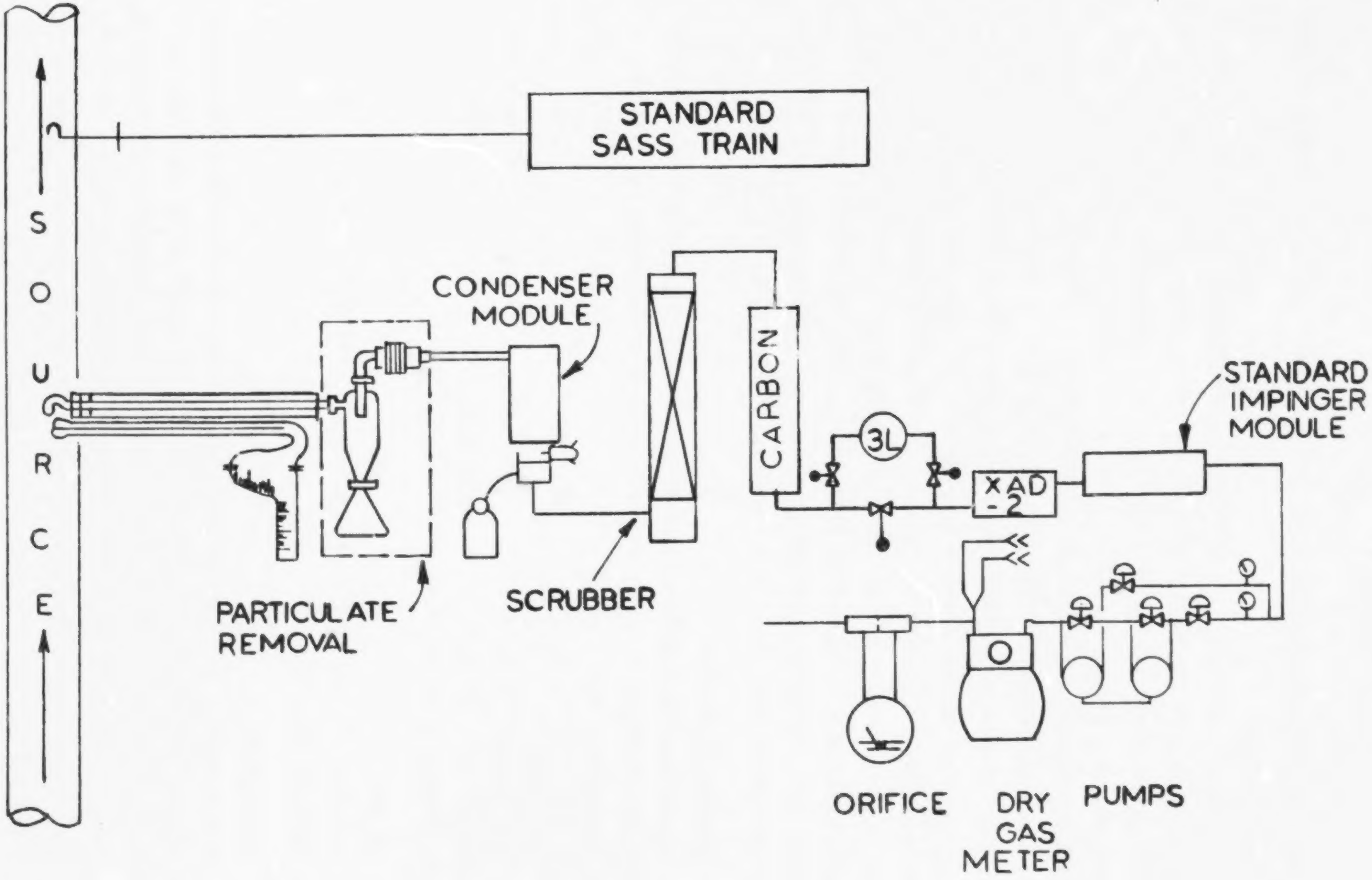
3.5.4 Reagents

The list of required reagents for the combined screening test is presented in Sections 3.3.4 and 3.4.4.

3.5.5 Preparation

See Section 3.2 before proceeding with screening train preparation.

Figure 12 shows the configuration of the train to be used for the combined scrubbing and carbon adsorption evaluation. Assemble the components of the train as shown. Detailed instructions for set-up of standard SASS train items are included in Reference 4. The following steps are necessary to prepare the train for sampling:



STANDARD SASS TRAIN
S O U R C E
CONDENSER MODULE
CARBON
3L
XAD -2
STANDARD IMPINGER MODULE
PARTICULATE REMOVAL
SCRUBBER
ORIFICE
DRY GAS METER
PUMPS

Figure 12. Combination scrubbing and carbon adsorption screening train.

1. Place a filter in the filter holder;
2. Fill the scrubbing solution reservoir with sodium carbonate solution (approximately 16 liters).
3. Place 130 gms of XAD-2 resin in the appropriate canister and seal;
4. Place approximately 5 kg of activated carbon into the carbon canister and seal;
5. Fill the standard SASS impingers with appropriate reagents;
6. Perform the standard leak test as required by Level 1 protocol, and replace or repair any components which do not meet leak testing requirements; and
7. Transport the equipment to the test site.

Arrangements should be made at this time for gathering of process operation data during the sampling period. Be sure that an adequate supply of ice is available (each train may require as much as 100 lbs/hr during the sampling period). Using the preliminary data obtained in Section 3.2 of this procedure, calculate the required sampling nozzle size and sample flow rate, as shown in Reference 4. Attach the nozzle to the probe and perform a leak test to assure that the equipment was not damaged during transportation to the site. Turn on the scrubber solution recirculation pump and set the flow to approximately 1 liter/minute. Energize all components which require heating/ cooling, i.e., probe, cyclone oven, gas cooling device. When these components have attained the designated temperatures, proceed to Section 3.5.6.

3.5.6 Sampling Procedure

Place the probe in the stack and position the nozzle at the point of average velocity. Record all necessary train operation data (gas meter reading, temperatures, stack gas flow rate). Start the pumps and set the sampling flow rate to the proper value as calculated from the average velocity data. Operate the train until a minimum of 1,000 cubic feet of gas has been sampled, as indicated by the gas meter. If particulate build-up causes a severe increase in vacuum and corresponding drop in sample flow rate, the test must be halted to replace the filter. The scrubbing solution should also be replaced at this time. Monitor the temperatures through the condensate trap and the impinger train and the pH of the scrubbing solution. A pH of less than ten is not acceptable and the scrubber solution should be replaced if the pH drops below this value. Condensate will build up in the trap and must be transferred periodically to the condensate collection bottle. The detailed procedure is shown in Reference 4.

Toward the end of the sample run (900 to 1000 ft^3 sampled) a 3-liter grab sample will be taken for GC analysis. This is accomplished by placing a 3-liter sampling bulb in line and momentarily diverting the gas flow through the bulb (Refer to Figure 9). Open valves 2 and 3 and then close valve number 1. Leave the valves in this position for one minute to ensure proper flushing of the sample container. After the sample has been taken, open valve 1 and close valves 2 and 3. Remove the bulb from the line and transport to the van for GC analysis. Level 1 procedures are used to analyze for low-molecular weight hydrocarbons in this sample.

When sufficient sample volume has been collected by the train, shut down the pumps by first closing the coarse control valves. When the vacuum gauge has dropped to zero, the pump switches may be turned off. Record the final gas meter reading and all temperature readings.

3.5.7 Sample Handling Procedures

Remove the probe from the stack and turn off all heating/cooling elements. Opening the oven door will speed cooling of the oven and contents. Stop circulation of scrubbing solution. Remove the XAD-2 cartridge, seal the ends, tag the sample and submit for Level 1 analysis. Remove the cyclone and filter assembly, discard the collected particulate matter and clean all surfaces. Remove the silica gel from its canister and clean the container. Transfer the condensate sample to a separatory funnel. Using a pH meter, adjust the pH to 7.0 with ammonium hydroxide or hydrochloric acid. Extract the sample with three 50-ml portions of methylene chloride. Tag this sample and submit as "Organic Extract". Divide the remaining aqueous sample into two equal parts. Using a pH meter, adjust each part as follows:

Part A - Acidify to pH less than 2 with nitric acid.
Part B - Adjust pH to 12 with sodium hydroxide.

Transfer each part to a suitable size polyethylene bottle for shipment to the home laboratory.

The spent sodium carbonate solution and the spent carbon may be discarded at this time.

SECTION 4
SOLIDS METHODOLOGY

4.1 BACKGROUND

Solid wastes generated at coal conversion plants may be the most variable of the multimedia discharges, both in form and composition. They usually consist of highly concentrated pollutants combined in residues from wastewater and gas treatment technologies in addition to the unwanted materials present in coals, minerals and ores processed for fuel value and/or metal content. Types of waste solids include:

1) Residues from the conversion processes including accompanying unrecovered carbon or hydrocarbons;
2) Residues from coal combustion processes/power generation;
3) Spent catalysts from shift conversion, methanation or catalytic synthesis reactors, liquefaction reactors, hydrotreatment and liquids products upgrading (e.g., reforming and hydrocracking);
4) Tar and oil sludges;
5) Filter precoat materials and filtered solids; and
6) Solids and sludges from air/water pollution control operations.

Not included above are solids which are often utilized as marketable byproducts and do not require further treatment or consideration for final disposal. An example is elemental sulfur recovered from gas cleanup processes such as Claus and Stretford. Similiarly, many catalysts are of significant value to justify regeneration for recycle. In such cases, air emissions and/or wastewaters are usually produced.

Comparatively few options are available for the safe disposal of solid materials containing toxic or problem components. Principally, these are incineration, fixation or encapsulation, and landfilling. Landfilling is normally the ultimate means of final disposal. Incineration usually produces an ash, and often a sludge when scrubbing for emission control is required.

These residues require final disposal such as landfilling. Fixation and encapsulation processes typically treat the solid to produce an inert (relatively non-leachable) material suitable for final disposal. Solids which have stable characteristics or which are considered harmless to the environment may be landfilled without treatment or utilized for construction materials and land reclamation. If pollution from leachate is a possibility, a controlled landfill area (with an impermeable bottom liner and a runoff-collection system) will be required.

4.2 SCREENING PROCEDURES

4.2.1. Applicability

Incineration of solid wastes can take several forms such as high temperature thermal destruction, catalytic destruction, pyrolysis and wet air oxidation. It is impractical to consider outfitting a mobile CAD test facility with bench scale equipment to evaluate the effects of these types of processes. Sampling and measurement of residue and resultant stack gases are difficult and costly and may not yield useful data unless the test is run under the (larger scale) conditions employed in incineration studies used to develop design criteria for scale-up.

Chemical fixation of encapsulation techniques are proprietary in nature and could not be satisfactorily duplicated in a CAD facility. Samples would have to be forwarded to a selected process vendor if data are to be developed. This approach is not reasonable until Level 1 S/A data establish the need for treatment.

Based on the foregoing factors, CAD evaluation of the effects of incineration and fixation/encapsulation as solids handling/disposal techniques using screening test procedures is not included in the CAD program. An additional Level 1 S/A test is recommended (Section 4.2.3).

The CAD solids methodology does not incorporate a screening procedure for generating leachate from solids or semi-solids slurries. A review of the published literature showed that the practices and techniques reported by other investigators were generally too long in testing time to be considered for CAD. Also, there was considerable subjectivity in the approaches employed by each researcher. Suggested testing for leachate are shown in Sections 4.2.2. and 4.2.3.

4.2.2. Current Testing

Primary concerns connected with solids disposal by landfill are the quantity and quality of the leachate, and its subsequent effect on subsurface waters (presuming the landfill is unlined). Leaching tests to generate a water sample are specified in Level 1 S/A protocols and need not be performed in the field as part of CAD. Two leachate samples are developed in Level 1: one from extraction with deionized water, and a second using dilute hydrochloric acid solution. It is recommended that data from these determinations (with suggested supplemental testing) be used for evaluation of leachate impact on the environment. If adverse effects on groundwater are shown to be likely, an impermeably lined basin will have to be anticipated (conceptually) and leachates processed as an aqueous waste stream.

4.2.3 Supplemental Testing

As an addition to the leachate testing currently performed under Level 1 S/A procedures (Section 4.2.2), it is recommended that a third leaching medium be added. The extractant should be a dilute alkaline solution, such as ammonium hydroxide. The purpose of this is to produce a leachate which might result if the solids were in contact with alkaline conditions at a landfill site.

Another test not presently indicated in Level 1 S/A procedures is the determination of the fuel value of a solid. When considering incineration as a potential treatment technology, it is necessary to know the fuel value in order to evaluate the economics of the option and get an indication of supplementary fuel requirements. Fuel value is easily determined using standard methods and a bomb calorimeter.

The Level 1 S/A sample size of one (1) kilogram presently specified should be sufficient to accommodate the additional heat value testing recommended.

Although not included in CAD procedures at this time because of its tentative status, reference is nevertheless made to an "Extraction Procedure" (EP) proposed by the EPA for developing leachates from toxic wastes (Federal Register; Vol 43; No. 243; Dec. 18, 1978). If the EP is eventually adopted as a standard investigative procedure, it will be a candidate for inclusion in the CAD solids methodology in the future.

SECTION 5

LABORATORY VERIFICATION

During the formulation of Control Assay Development (CAD) methodologies, it became apparent that certain methods should be verified in the laboratory before being adopted for use in the final procedures.

The objectives of the laboratory study were:

1. To determine logistical problems of sample handling;
2. Assess the adequacy of the proposed designs and operation of appropriate test units;
3. Verify the use of a dry bacterial culture for biological oxidation studies; and
4. Evaluate the feasibility of using SASS components for air testing.

CAD field procedures for coal conversion wastewater treatment require the processing of relatively large volumes of water as compared to standard process development testing procedures for determining treatability of a given waste. Volumes of 400 liters or more have to be processed to accommodate normal system requirements and to make samples available for IERL Level 1 analyses which require 10 liters from each unit process tested. Figure 13 indicates the processes initially selected for testing wastewater by CAD methods.

To accomplish the proposed objectives for the wastewater treatment portion of CAD, a 200-liter synthetic wastewater sample was processed as it would be by a sampling team in the field. Level 1 analytical procedures were not applied to the treated samples because of time and cost restrictions. Rather, traditional wastewater parameters (COD, BOD, solids and metals analyses) were used to measure/monitor the performance of each unit process. Separate studies were conducted to determine the effectiveness of using dry bacteria versus an acclimated activated sludge for the biological oxidation assessment.

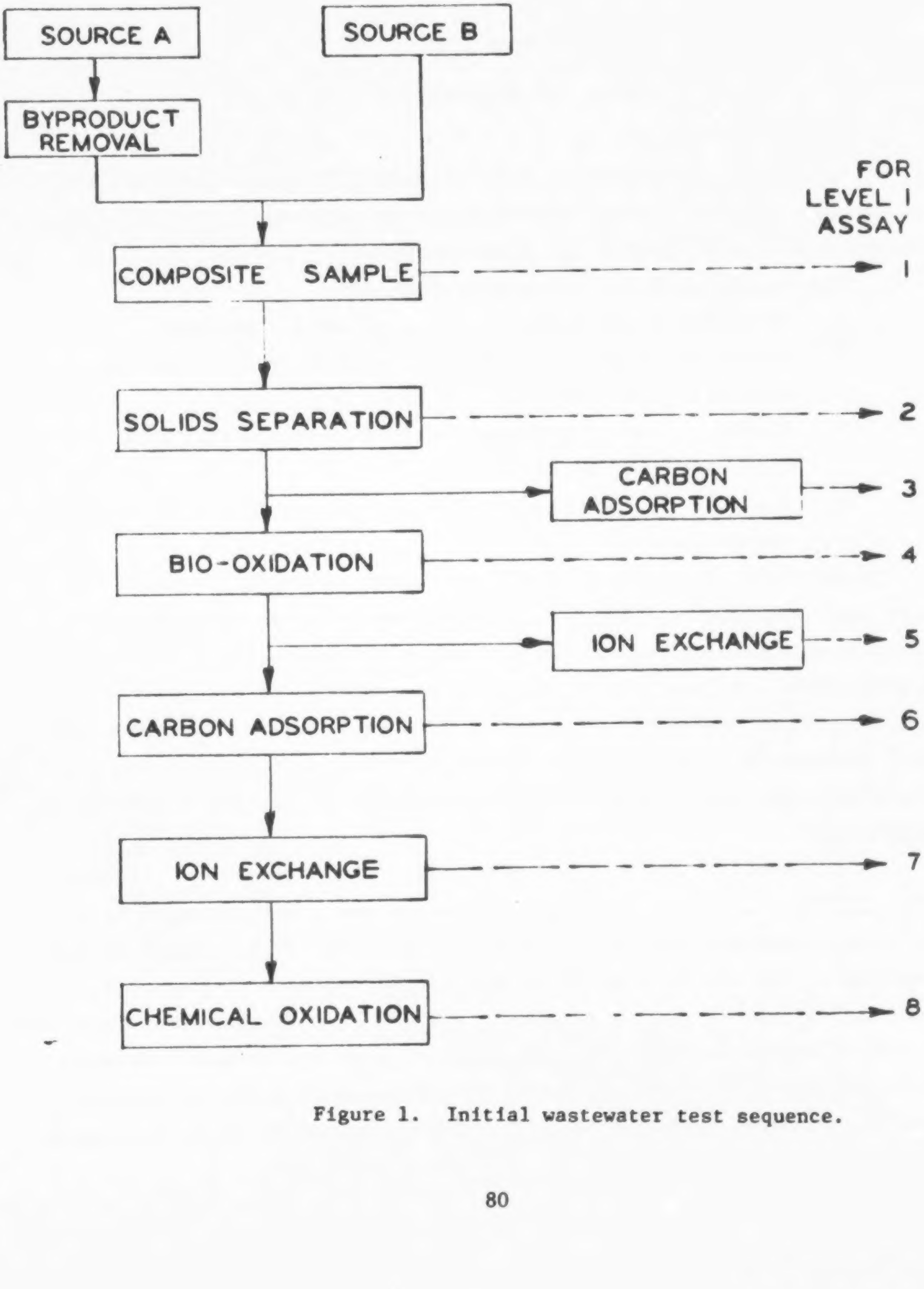

SOURCE A
SOURCE B
BYPRODUCT REMOVAL
FOR LEVEL I ASSAY
COMPOSITE SAMPLE
1
SOLIDS SEPARATION
2
CARBON ADSORPTION
3
BIO-OXIDATION
4
ION EXCHANGE
5
CARBON ADSORPTION
6
ION EXCHANGE
7
CHEMICAL OXIDATION
8

Figure 1. Initial wastewater test sequence.

CAD air methodologies specify the use of a modified Source Assessment Sampling System (SASS). The minimum sample volume required by IERL Level 1 air analyses for particulates, organic and inorganic materials is 1000 cubic feet. This volume allows for collection of sufficient quantities of trace components to reach detectable levels.

In order to evaluate the feasibility of modifying a SASS train for CAD purposes, a unit was borrowed and subjected to various tests to determine whether the system would have enough inherent capacity to cope with an increased pressure drop caused by supplemental CAD testing modules. Several tests were conducted using a prepared gas mixture to verify the efficiency of the proposed scrubbing unit and the carbon adsorption canister. Figure 19 indicates the air screening tests required by CAD methodologies.

This report summarizes the results and conclusions of the laboratory verification studies for both air and water methodologies.

SECTION 6

WASTEWATER SCREENING

6.1 SYNTHETIC WASTEWATER COMPOSITION

Because of the difficulty of obtaining an actual coal conversion process waste, it was decided to use a synthetically prepared waste for the laboratory verification studies. The organic portion of the synthetic wastewater used for verification purposes was derived from a formulation developed by Dr. Philip Singer from research conducted at the University of North Carolina at Chapel Hill[5]. The concentrations of organic compounds proposed by Dr. Singer defined a coal gasification wastewater with no byproduct recovery steps. Since the laboratory verification was intended to test CAD methodologies after byproduct recovery, the initial organic concentrations were modified to simulate a phenol recovery step. The Phenosolvan® process was selected as a typical phenol extraction process. Extraction recoveries expected from this process were estimated to be[6]:

99.5% for monohydric phenols
60.0% for polyhydric phenols
5.0% for other organics

The phenolic compounds listed for waste A (Table 6) were segregated by chemical structure, and values of 90% and 50% removal were used to calculate the concentrations remaining after byproduct recovery of monohydric and polyhydric phenols, respectively. No concentration adjustments were made for "other organics."

The inorganic components of the synthetic mix were selected after reviewing actual sample data from several operating plants. Table 7 lists the target inorganic concentrations in the synthetic mixture.

TABLE 6

ORGANIC COMPOSITION OF SYNTHETIC WASTE

Compound		Waste A Concentration mg/l	Synthetic Waste Concentration mg/l
1.	Phenol	2000	200
2.	Resorcinol	1000	500
3.	Catechol	1000	500
4.	Acetic Acid	400	400
5.	o-Cresol	400	40
6.	p-Cresol	250	25
7.	3,4 Xylenol	250	25
8.	2,3 Xylenol	250	25
9.	Pyridine	120	120
10.	Benzoic Acid	100	100
11.	4-Ethylpyridine	100	100
12.	4-Methylcatechol	100	50
13.	Acetophenone	50	50
14.	2-Indanol	50	-
15.	Indene	50	50
15.	Indole	50	50
17.	5-Methylresorcinol	50	25
18.	2-Naphthol	50	50
19.	2,3,5 Trimethylphenol	50	5
20.	2-Methylquinoline	40	40
21.	3,5 Xylenol	40	4
22.	3-Ethylphenol	30	3
23.	Aniline	20	20
24.	Hexanoic Acid	20	20
25.	1-Naphthol	20	20
26.	Quinoline	10	10
27.	Naphthalene	5	5
28.	Anthracene	0.2	0.2

TABLE 7

INORGANIC COMPONENTS OF SYNTHETIC WASTE

Component	Concentration (mg/l)
F	2.0
Fe	0.2
Pb	0.04
Hg	0.007
PO_4	2.5
S	12.0
Zn	0.08
As	0.2
Cd	0.02
Cr	0.03
Cu	0.1
CN^-	1.0

One major problem encountered with the use of the synthetic wastewater mixture was noted early in the study was a loss of COD organics on standing. This situation is discussed in the "Biological Oxidation" section of this report.

A second phenomenon observed during CAD verification testing was the continued precipitation of solids in the synthetic waste as it aged.

The foregoing situations prompted appropriate revisions in the Control Assay (CA) screening procedures and CAD methodologies initially conceived.

6.2 SOLIDS SEPARATION

6.2.1 Initial Concepts

The removal of suspended solids from a wastewater sample (Primary Treatment) may be accomplished by several methods. They can include: chemical coagulation and flocculation, gravity separation, physical straining, centrifugation, and filtration through granular media. Suspended solids removal for CA screening requires only that solids be removed to a level that will not interfere with subsequent unit operations.

Jar tests using chemical coagulants are a common laboratory procedure for solids separation. However, these tests can be time consuming because of the need to evaluate various types and combinations of flocculants. In addition, the flocculants eventually selected can chemically alter the composite wastewater test sample, thereby adding unnecessary constituents to the IERL Level 1 analysis samples. Consequently, solids separation via chemical treatment was discounted as not being attractive as a CA screening procedure.

Four candidate approaches were considered for separation of solids by physical means; centrifugation, sand filtration, microstraining, and cartridge filtration. Although it was felt that all the above physical separation methods would be applicable, the first three were discarded after evaluation of various factors including: degree of solids removal required; the kind of specialized apparatus needed; the question of logistics for storing, transporting, and obtaining new filter media; the ease of operation; and the reproducibility of results.

6.2.2 Selected Alternative

Filtration of the composite sample using a polypropylene cartridge was deemed to be the most favorable method for solids removal in the CA screening procedure. A pore size of 75 microns was selected as being descriptive of the particle size discharged from a well-designed primary settler.

6.2.3 Test Work

A 200-liter sample of synthetically prepared waste was passed through the cartridge filter with no difficulty. The synthetic waste typically had a fairly low suspended solids level at the outset and no problems with filter plugging were encountered. It was noted, however, that the waste did exhibit a tendency to precipitate solids from solution upon standing.

Several filtrations were made at various times during the laboratory study and the 200-liter sample could be passed through the filter in 15 minutes or less using a standard laboratory pump. The aeration which occurred due to the pumping action caused some foaming in the sample, but this situation was not considered to be a significant problem.

6.2.4 Discussion of Results

It is possible that actual wastewater samples will have a much higher level of solids than was encountered in the synthetic waste. Also, during chemical pretreatment for byproduct recovery, conditions could develop under which precipitates might be formed, thereby increasing the total amount of suspended solids in the sample. Laboratory verification testing did not include the byproduct removal steps embodied in the CAD test sequence (Figure 13).

The filter cartridges are relatively inexpensive and easy to change when their filtering capacity has been exhausted. It would be possible to make several filter changes during a run, if it became necessary, without a significant loss of time. Cartridge filters are also available in various pore sizes, and two or more filters of gradually decreasing size could be used in series to obtain a higher degree of solids removal, if required. The synthetic waste had no visible effect on the integrity of the cartridge or the filter holder (both polypropylene). Solids removal by cartridge filtration is recommended for use in CA screening procedures.

6.3 CARBON ADSORPTION

6.3.1 Initial Concepts

Removal of soluble organic compounds by activated carbon adsorption is encountered with increasing frequency as a process for wastewater treatment. Carbon installations exist whose purposes range from use as a polishing step for removal of trace concentrations of pollutants, to facilities for pretreatment of waste at source prior to further processing. Compounds exhibiting highly polar properties and having relatively high molecular weights are generally most amenable to removal by activated carbon.

Evaluation of the effects of activated carbon as a unit operation involves selection of a particular carbon; measurement of adsorptive capacity using batch isotherms; and development of a breakthrough curve and regenerability characteristics as determined from a continuous-flow pilot column test. In a detailed concept design study, a number of different carbons are examined using a particular wastewater before the best candidate is selected for the column tests. Considering the basic purposes for CA screening procedures and the field time constraints imposed, the use of a single, somewhat broad-based carbon is proposed. This approach may not produce data using the best-suited carbon, but the results will be sufficiently indicative of the applicability of carbon as a treatment step, and will still keep the investigations within the bounds of logistic practicality.

Since it is a relatively simple matter to perform carbon isotherms on wastewater samples in the field to determine the approximate organic loading and optimum pH conditions for a specific wastewater, they are included as a CA pre-screening procedure. Results of isotherm testing provide useful guidelines for the column test runs, in addition to the data they furnish directly.

Two methods were considered for treating the CA composite sample by activated carbon: (1) continuous feeding through a series of carbon columns; and (2) batch testing. Each batch treatment of a composite sample represents only one equilibrium condition. Also, it is anticipated that a microfiltration step for removal of suspended carbon fines would be necessary before subsequent CA processing steps could be performed.

Pilot column testing normally requires continuous sampling throughout the run at several points in the carbon system to determine wavefront movement

TABLE 8

ACTIVATED CARBON TEST RESULTS

CARBON ISOTHERM RESULTS

Carbon Dose (M) (gm/l Sample) (*)	COD Remaining (C) (mg/l)	COD Removed (x) (mg/l)	X/M (mg COD/gm Carbon) (**)
0	5000	0	0
1	4653	347	347
5	3931	1069	214
10	3657	1343	134
20	3259	1741	87
50	1866	3134	63
100	1000	4000	40

(*) Corrected for 100 ml sample size used.
(**) Equivalent to lb. COD adsorbed/1000 lb. Carbon.

CARBON COLUMN TEST RESULTS

Run Number	Linear Flow Rate (ml/min.)	Loading Rate (gpm/ft^2)	Influent Concentration		Effluent Concentration (+)		% Removal	
			COD mg/l	BOD mg/l	COD mg/l	BOD mg/l	COD	BOD
1A	190	2.3	6864	2200	1714	440	75	80
1B	190	2.3	1714	440	334	186	80	58
1 (A&B)	190	2.3	6864	2200	334	186	95	91
2	200	2.4	3581	1940	347	197	90	90

(+) Corrected for dilution water in columns.

and breakthrough, which are among the data needed for an actual column design. Since only a limited number of samples can be taken during CA testing, it is not proposed, nor is it necessary, to conduct this detailed type of design study for a Level 1 CA screening.

6.3.2 Selected Alternative

Based on the foregoing considerations, continuous column operation was selected for use in CA screening procedures. However, the number of samples to be collected was limited to the initial feed and the final effluent. The volume of the initial feed to the carbon system will be the amount needed to produce the analysis samples after the carbon test as well as from any subsequent CA screening procedures, plus the amounts needed to displace "fill water" in the test units. The feed volume will be contained in a single vessel, pumped continuously through the carbon beds, and collected in another vessel at the effluent end. After withdrawing an aliquot sample for subsequent laboratory analysis, the remaining effluent becomes the influent for any CA screening steps to follow. To determine general column operation parameters, several isotherms are to be run on a small quantity of the feed sample prior to the continuous run.

6.3.3 Test Work

Table 8 summarizes the results of the activated carbon verification testing. A Freundlich isotherm was performed on the synthetic waste sample to establish the effectiveness of carbon treatment and to gain some insight into the amount of carbon required to produce acceptable organic removal rates. The standard COD analysis was used as a measure of organic removal. The values of X/M (quantity of COD adsorbed per unit weight of carbon) were calculated and plotted versus concentration of residual COD in solution, as shown in Figure 14. The plot of the data showed a definite break at carbon dosages of 20 gm/l and higher. The sudden change in slope indicated that two (or more) classes of organics are present, which are not uniformly adsorable.

Carbon column runs were made using the column design specified by the CAD wastewater methodology, namely, four 2-inch I.D. glass columns connected in series, each charged to the three-foot level with activated carbon (7.8 lbs of carbon). The test sequence for CAD (Figure 13) required the use of carbon at two points, before and after bio-oxidation. A synthetic wastewater was

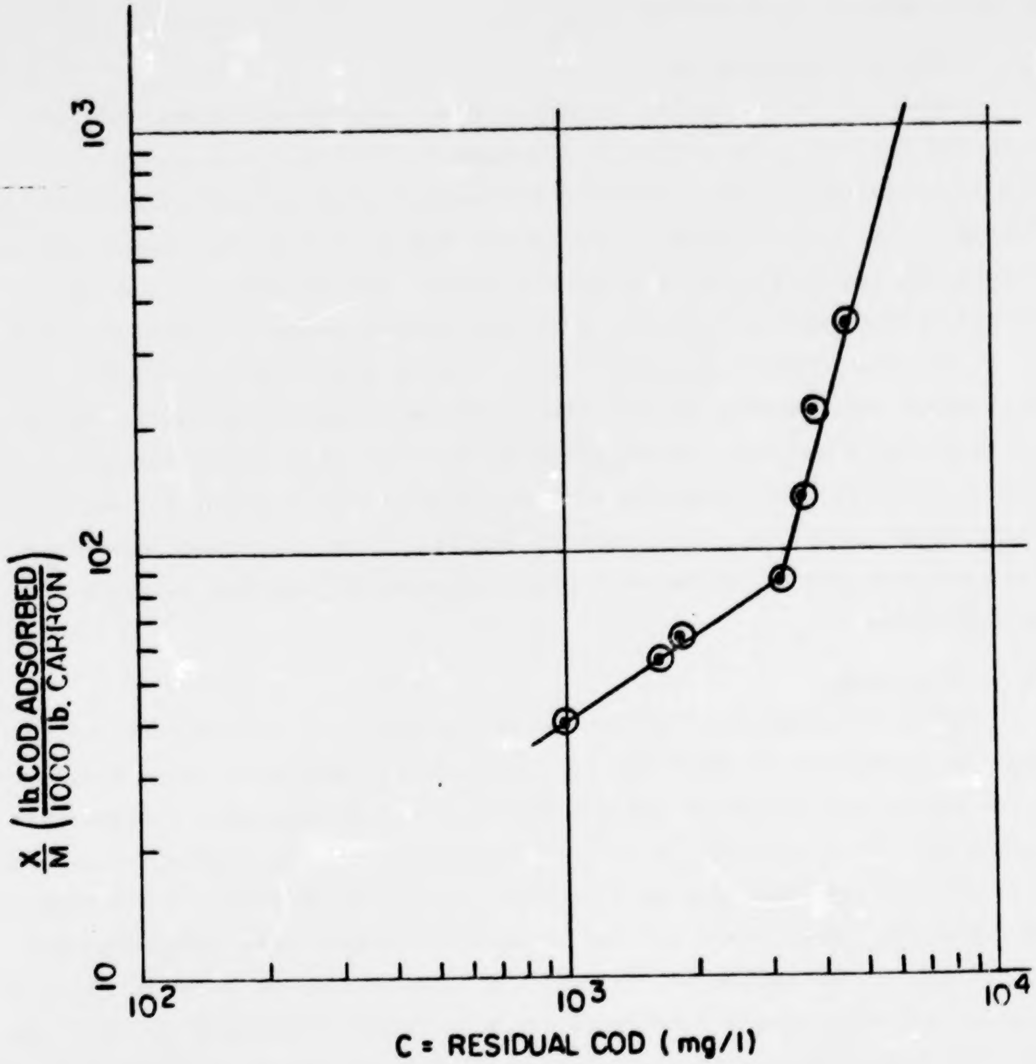


Figure 14 Carbon isotherm plot.

prepared in accordance with the compositions shown on Tables 6 and 7. After filtration (described in "Solids Removal"), the sample was equally divided (84 liters per each run) for use during the column tests.

In view of the apparent dual adsorption regimes demostrated by the batch isotherm (Figure 14),it was decided to collect data during the first test run in two stages. The 84 liters of filtered waste were pumped through fresh carbon in the columns, and the effluent retained (Run A). After rebedding the columns with new carbon, the effluent from Run A was used as the influent to Run B.

The second portion of synthetic waste was treated by the bio-oxidation CA screening procedure, and then fed to fresh carbon in the columns. Results of this test are indicated as Run 2.

6.3.4 Discussion of Results

To varying degrees, carbon is effective in reducing the COD and BOD of the synthetic waste sample in both applications. Referring to Table 8, it is seen that the combined Run 1 achieved essentially the same effluent COD and BOD concentrations and percent removals as Run 2. It must be recalled, however, that Run 1 was conducted in two stages and that twice the carbon was bedded. The specified CA screening procedures are more closely simulated by Run 1A (alone). The data show that substantially less (BOD/COD) organics are removed than in Run 2, which follows bio-oxidation.

It can be postulated that lower molecular weight organics were not retained in the four-column system but were captured in an eight-column set up (wavefront effect). Apparently, the four-column system was able to produce a better effluent quality after one pass by virtue of the reactions taking place during the bio-oxidation CA procedure (described in a later section).

The run time required to process a 95-liter sample through the four-column system at a superficial velocity of 2 to 3 gpm/ft^2 is approximately 8 hours. By increasing the column size to 3-inch I.D., the sample could be processed in slightly less than 3 hours at an identical superficial velocity. On the other hand, the amount of carbon available would be increased more than twice.

One disadvantage of increasing the column size is that the dilution factor from the "fill" water existing in the carbon bed at the beginning of the run becomes larger in relation to the size of the sample being passed through the columns. In any event, the dilution factor has to be considered when interpreting test results, and should not substantially affect the evaluation of activated carbon as a unit process, provided that a sufficiently large sample is processed.

The synthetic waste demonstrated a tendency to form some additional solids on standing, which were removed by the carbon bed. If real life wastes react similarly, it may be necessary to perform a supplemental cartridge filtration before feeding the sample to the columns to prevent bed blinding.

The column design was modified slightly, since plugging problems arose using the original fritted glass support materials. These were removed and replaced with 50-mesh screen which was satisfactory for all subsequent runs.

The new design will be incorporated into the CA methodologies together with the increased column diameter.

6.4 BIOLOGICAL OXIDATION

6.4.1 Initial Concepts

The original intent of wastewater treatment evaluation is to have a CAD field team on-site to perform all CA aqueous screening procedures in a time period of approximately one week. Standard biological treatability testing using activated sludge normally requires two weeks to a month of continuous operation for acclimation of the biomass to the specific waste being studied. After acclimation, an additional 3 to 4 weeks of data gathering under steady state conditions are required to provide system performance and design parameters for that particular wastewater. CA screening procedures are not developed for the purpose of obtaining design data, therefore, the continuous sampling after acclimation is not necessary. However, to properly evaluate a biological system as a unit process, it is imperative that an acclimated seed be used.

The requirement for an acclimated seed on-site posed several problems. A "wet" seed must be continuously aerated and provided with some type of feed substrate during transportation to a plant and while on location. The possibility of acclimating a sludge from a local municipal treatment plant was also considered. While being a viable option, such an approach could introduce unwanted contaminants to the system, depending on the type of industrial waste normally treated at the local plant. Biological sludge from a plant which normally treats coke oven wastes would be more ideal, since components of this type of wastewater are similar to many materials found in coal conversion wastes. However, the likelihood of always being in a location near this type of treatment plant would be small and could not be realistically incorporated into the screening methods. In essence, it was desirable to determine if there were any feasible alternatives to using a wet seed for the CA screening procedure.

By private communication, one investigator reports experimentation examining the possibility of quick-freezing activated sludge for subsequent use. While interesting, the work is still in an early trial stage and the results are too tentative for inclusion in a CA screening procedure at this time. A second alternative is the use of dry bacterial cultures which are offered commercially by several vendors.

Dry bacterial cultures are grown on an inert material. The organisms are selectively mutated and segregated in accordance with their ability to biologically degrade specific classes of compounds. One such culture is purported to specifically oxidize phenolic compounds, cyanides and various other similar contaminants. The culture is marketed in a dry powder form and, according to the vendor, the organisms are reactivated when added to warm water and aerated for 24 hours.

The dry bacterial culture route offers a potential solution for the transportation and acclimation problems posed by CA methodology.

6.4.2 Selected Alternative

It was decided to test a commercial dry bacterial culture to ascertain whether or not it would serve as a practical alternative for a wet seed, and/or to try to establish a relationship between system performance using dry bacteria as compared with a seed acclimated to a waste in the more usual manner.

6.4.3 Test Work

Various tests were performed to evaluate biological screening procedures. The tests were divided into two catagories: Batch testing and continuous systems. Additionally, experimental work was conducted (1) to gain a better familiarity with the characteristics and application of the dry bacterial culture; and (2) to explore some side issues that arose during the test work, which were relevant to the overall bio-oxidation CA verification procedures/CAD methodologies.

The batch tests were performed either in 2-liter glass beakers or in 7-liter cylindrical, stainless steel containers. Vessels used for the continuous systems testing were 7.5-liter capacity stainless steel tanks fitted with baffle plates at the outlet and to provide a quiescent zone for solids settling. The volume of the aerated portion of these tanks was about 6 liters.

An attempt was made to start a continuous system using the dry bacterial culture. After several days of feeding with dilute synthetic wastewater, there was no apparent biological growth. It was believed that the bacteria were present as a dispersed growth and were being lost in the effluent, since there was no measurable solids production in the system and effluent COD values were consistently higher than the feed analyses. Millipore filtration of the effluent samples did not significantly reduce the effluent COD results.

During this preliminary work, it was also noted that the COD values of the feed material, initially held in an open container, dropped markedly over a period of several days. Loss of volatiles to the atmosphere was strongly indicated.

Air stripping tests were performed on batch samples of the synthetic waste to quantify the COD material lost (presumably) by volatilization and/or oxidation of the organic compounds in the waste (Table 9A). At the same time, tests were conducted to determine the amounts of COD and BOD added to a batch system by the dry bacterial culture alone (Table 10). A supplemental air stripping/oxidation run was conducted near the end of the laboratory test, examining the effect of volume on BOD/COD reductions. For convenience, these data are shown on Table 9B. Results of the foregoing test work will be discussed later.

The supplier's recommended standard procedure was followed for reactivating the dry bacterial culture. First, a measured amount (25 gms) of bacteria/substrate material was added to three liters of distilled water and heated to 38°C (100°F) and mixed for two hours. The batch was then aerated

TABLE 9A

AIR STRIPPING/OXIDATION TESTS

Aeration Time (hrs)	Run #1		Run #2		Run #3				Run #4			
	COD (mg/1)	Rem. %	COD (mg/1)	Rem. %	COD (mg/1)	Rem. %	BOD (mg/1)	Rem. %	COD (mg/1)	Rem. %	BOD (mg/1)	Rem. %
0	5660	0	5504	0	4761	0	3306	0	4280	0	2340	0
1	4228	25.3										
2	2686	52.5										
4	2412	57.4										
24	1965	65.3	2046	62.8	2637	44.6	1408	57.4	3412	20.0	1980	15.4
48			1450	73.7	2030	57.4	960	71.0	2410	43.7		
72			1580	71.3	1834	61.5	760	77.0	2222	48.1	1200	48.7

NOTE: Sample volume used was 1.5 liters.

TABLE 9B

EFFECT OF VOLUME ON AIR STRIPPING/OXIDATION

		Run #5- 22 gal. Volume				Run #6- 7 liter Volume			
		Aeration Only		Dry Bacteria		Aeration Only		Dry Bacteria	
Parameter	Infl. (mg/1)	Effl. (mg/1)	Rem. (%)	Effl. (mg/1)	Rem. (%)	Effl. (mg/1)	Rem. (%)	Effl. (mg/1)	Rem. (%)
BOD	1080	780	27.8	740	31.5	780	27.8	870	18.4
COD	7560	5520	27.0	5680	24.9	3760	50.3	3840	49.2

NOTE: 24 hours aeration period on all units

TABLE 10

DRY BACTERIA-COD AND BOD DATA

BOD

	Dry Bacteria Concentration								
Aeration Time (hours)	0.75 gm/1	Adjusted Value*	1.5 gm/1	Adjusted Value*	2.25 gm/1	Adjusted Value*	3.0 gm/1	Adjusted Value*	Average Adjusted Value
24	44	59	92	61	290	128	386	128	94
48	60	80	112	75	274	121	268	89	91
72	86	115	106	71	140	62	314	104	88

Average BOD increase: 91 mg/1/gm Dry Bacteria added

COD

	Dry Bacteria Concentration								
Aeration Time (hours)	0.75 gm/1	Adjusted Value*	1.5 gm/1	Adjusted Value*	2.25 gm/1	Adjusted Value*	3.0 gm/1	Adjusted Value*	Average Adjusted Value
24	80	107	165	110	490	217	722	240	169
48	102	136	177	120	500	222	725	242	180
72	245	327	280	187	578	256	895	298	267

Average COD increase; 205 mg/1/gm Dry Bacteria added

*Mathematically adjusted to a Dry Bacteria concentration of one mg/1.

for 24 hours and aliquots were taken to produce various concentrations for analysis. The test results (Table 10) indicated that BOD and COD material is added by the dry bacterial culture. COD actually increases with aeration over a period of hours while the BOD concentration remains fairly constant. These relationships are depicted on Figure 15 .

The zero hour time did not include the initial 24-hour aeration period, therefore, the total aeration time from start of reactivation to the end of the test was actually 96 hours. These tests indicated that the substrate material will provide the bacteria with an adequate nutrient supply for at least 72 hours, while also adding organic food (COD) material to the system. Measurements of oxygen uptake rates on similar systems confirmed the continued high biological activity over the same time period.

Dry bacterial cultures can also be used as an additive to an existing biological system. Since poor results were being obtained from the continuous system, this operation was discontinued and replaced by two new continuous units, each containing biomass taken from a coke oven waste treatment plant. Identical amounts of the synthetic waste were fed to each of the units. Additionally, doses of the dry bacterial culture were introduced to one of the units on a daily schedule prescribed by the supplier's instructions. Gradually decreasing amounts of dry culture were added to this system until a "maintenance" dosage level (2 grams per 6 liters) had been reached. This dosage was continued for the duration of the testing period. Sludge from these units was later used for additional batch tests. Results of the continuous reactor testing will be discussed later in this report.

6.4.3.1 Batch Testing--

Three sets of batch tests were conducted, each set consisting of four batch reactors aerated for 72 hours. Samples from the reactors were taken every 24 hours and analyzed for COD, BOD and suspended and volatile solids. Air flow to each system was stopped for one hour before sampling to allow for solids settling. One reactor (Unit #1) in each series contained wastewater only (no biologically active seed introduced) for the purpose of comparing the effects of air stripping/oxidation of the waste to biological oxidation. The contents of the other three reactors were prepared as follows:

Unit #2 - Wastewater plus coke oven sludge (from continuous Unit A)

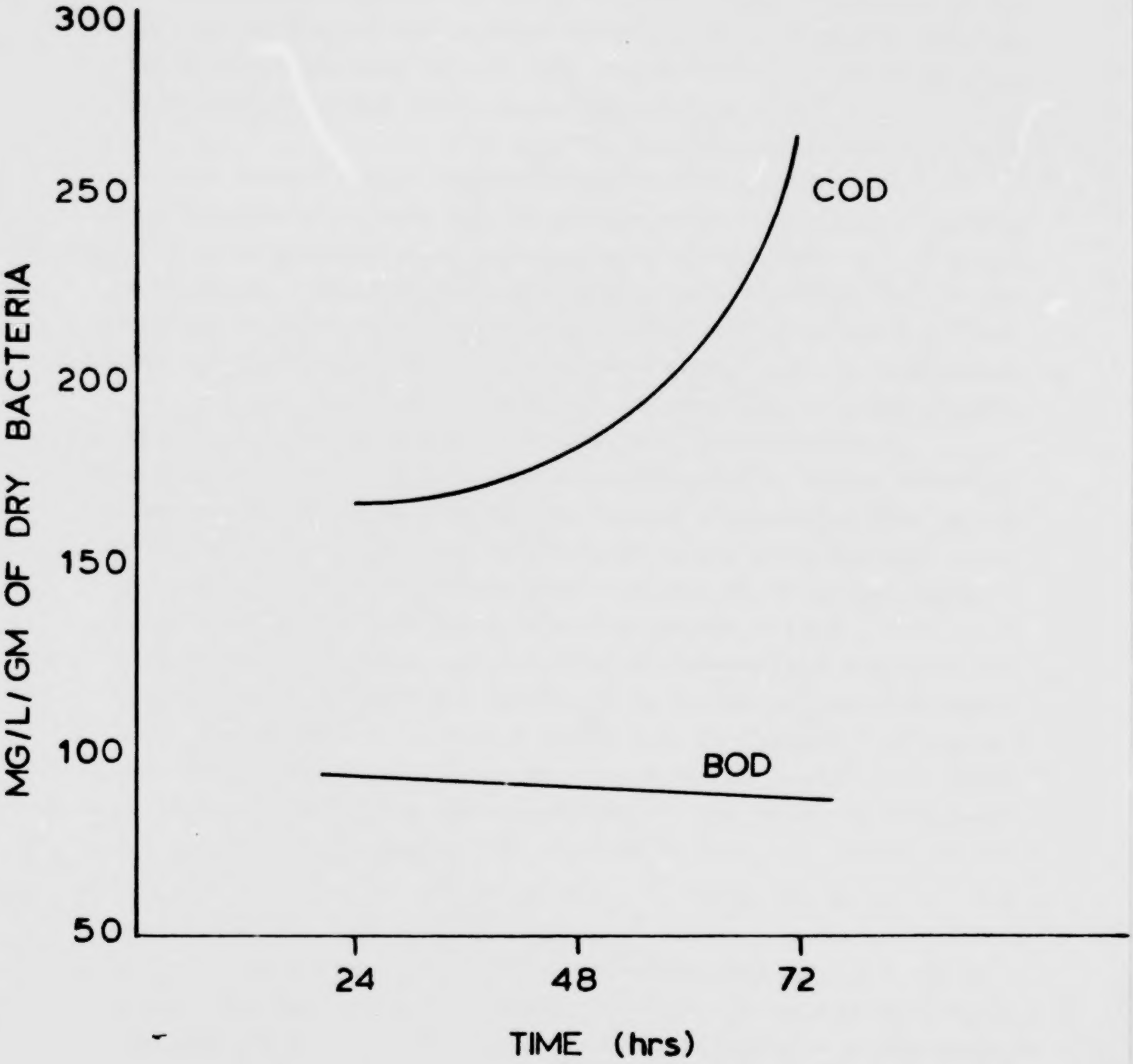


Figure 15. COD and BOD addition by dry bacteria.

Unit #3 - Wastewater plus coke oven sludge with dry bacteria (from continuous Unit B)

Unit #4 - Wastewater plus dry bacteria

Results of these batch tests are summarized in Table 11

6.4.3.2 Continuous Units--

Two continuous units were set up and operated for approximately 2 1/2 months. Both units (A and B) were seeded with a coke oven sludge, and one unit (Unit B) also received a daily dose of dry bacteria. The systems were contained in identical stainless steel reactor tanks each having a removable baffle to aid in clarification of the effluent streams. The influent to both systems was from a common tank and various concentrations of synthetic wastewater were used as the feed material. Initially, the synthetic waste was diluted to one tenth of the original strength and later changed to one quarter strength. During the final three weeks of testing both units were fed full strength synthetic wastewater.

Tables 12 and 13 show all data obtained from the continuous units. Figure 16 plots the influent and effluent COD data for both units over the entire testing period.

During the acclimation period (dilute waste feed), Unit B had consistently lower COD removals for the first month. From the thirty-fifth to the fiftieth day, both units operated very similarly. The full strength feed was started and Unit B showed an obvious performance advantage over Unit A, at least initially.

6.4.3.3 Control Assay Batch Test--

An 84-liter sample (22 gallons) previously treated for solids removal was subjected to the original CA screening procedure for bio-oxidation. This involved reactivation of dry bacteria and aeration with the waste for 24 hours. The dry bacterial culture concentration was 1.5 gm/liter. Results of this test are summarized below:

Influent					Effluent					% Removal	
COD	BOD	SS	VSS	pH	COD	BOD	SS	VSS	pH	COD	BOD
6864	2200	117	71	7.9	3571	2110	362	271	7.6	48.0	4.1

Note: Except for pH, influent and effluent concentrations are expressed as mg/1.

TABLE 11

BIOLOGICAL OXIDATION

BATCH REACTOR RESULTS

	Unit #1-Air Stripping/Oxidation			Unit #2-Coke Oven Sludge			Unit #3-Coke Oven Sludge + Dry Bacteria			Unit #4-Dry Bacteria			Aeration (hrs)
	Influent	Effluent	% Removal	Influent	Effluent	% Removal	Influent	Effluent	% Removal	Influent	Effluent	% Removal	
BOD (mg/l)	2823	1694	39.9	2520	1120	55.5	2630	1260	52.1	2570	1330	48.2	24
COD (mg/l)	4848	2698	44.3	4806	2078	56.7	4886	2368	51.5	4860	2162	55.5	
BOD (mg/l)	2823	960	65.9	2520	930	63.1	2630	660	74.9	2570	1130	56.0	48
COD (mg/l)	4848	1980	59.1	4806	1584	67.0	4886	1467	70.0	4860	2043	57.9	
BOD (mg/l)	2823	980	65.3	2520	510	79.7	2630	540	79.4	2570	840	67.3	72
COD (mg/l)	4848	1879	61.2	4806	1404	70.7	4886	1275	73.9	4860	1577	67.5	

NOTES

Unit #1 contained 1.0 liter tapwater plus 4.5 liters of waste.
Unit #2 contained 1.0 liter of activated sludge from continuous Unit A plus 4.5 liters of waste.
Unit #3 contained 1.0 liter of activated sludge from continuous Unit B plus 4.5 liters of waste.
Unit #4 contained 1.0 liter of reactivated dry bacteria (8.75 gms/l) plus 4.5 liters of waste.

TABLE 12

CONTINUOUS BIOSYSTEM TREATABILITY DATA

UNIT A

	Mixed Liquor (*)					Influent				Effluent			
Date (1978)	Temp (°C)	SS (mg/1)	VSS (mg/1)	DO (mg/1)	DO UPT (mg/1/hr)	COD (mg/1)	BOD_5 (mg/1)	SS (mg/1)	VSS (mg/1)	COD (mg/1)	BOD_5 (mg/1)	SS (mg/1)	VSS (mg/1)
8/8		2492	2336	7.6	16	58		11		415		25	25
8/9		2070	1950	7.6	14	490		4		593		415	390
8/10		2020	1850	8.0	5	375		4		686		360	334
8/11		1840	1716	7.6	4	307		28		400		84	82
8/14		1304	1184	7.4	4	82	30	23		226	51	4	
8/15		1368	1312	7.4	5	442		22		164		56	
8/16		1192	1088	7.4	4	130		254		144		102	
8/17		1104	1052	7.6	4	770		19		265		60	
8/18		1124	1036	7.4	5	575		59		147		10	
8/21		1044	944	8.1	3							14	
8/22													
8/23		976	864	8.1	3	890		16		126		24	
8/24		1012	884	7.4	6	822		40		174		22	
8/25		998	906	7.8	4	750	442			208			
8/28		1048	932	7.8	3.6			118		165		34	
8/29		1064	960	8.0	0	1251		34		146		136	
8/30		972	880	8.0	7	1138				121		116	
8/31		776	712	8.0	6	1087				104			

(*) Coke oven activated sludge only

TABLE 12 (Con't)

CONTINUOUS BIOSYSTEM TREATABILITY DATA

UNIT A

	Mixed Liquor (*)					Influent				Effluent			
Date (1978)	Temp (°C)	SS (mg/1)	VSS (mg/1)	DO (mg/1)	DO UPT (mg/1/hr)	COD (mg/1)	BOD_5 (mg/1)	SS (mg/1)	VSS (mg/1)	COD (mg/1)	BOD_5 (mg/1)	SS (mg/1)	VSS (mg/1)
9/5				8.6	6	834				97			
9/6		720	720	8.2	6	831				97			
9/7		812	784	7.2	7	913				90			
9/8	16	792	766	9.5	2.4	716	306			73	3		
9/11	21	868	737	8.0	7	542	294	30		98	0.6	58	
9/12	24	714	702	8.6	6		246				0.6		
9/13	20	682	594	8.8	4		206			85	0.6		
9/14							176				2.2		
9/15	21	600	508	8.0	5	519	104	56		81		42	
9/18	26	760	612	7.6	8	748							
9/19	21	1176	764	8.8	2.4	901				53			
9/20	21	772	604	8.4	5	1201				46	6	24	10
9/21	25			7.6	14	1031							
9/22	25	656	576	7.4	14	1005				75			
9/25		460	340			913				53			
9/26						854				55			

(*) Coke oven activated sludge only

TABLE 12(Con't)

CONTINUOUS BIOSYSTEM TREATABILITY DATA

UNIT A

	Mixed Liquor (*)					Influent				Effluent			
Date (1978)	Temp (°C)	SS (mg/1)	VSS (mg/1)	DO (mg/1)	DO UPT (mg/1/hr)	COD (mg/1)	BOD_5 (mg/1)	SS (mg/1)	VSS (mg/1)	COD (mg/1)	BOD_5 (mg/1)	SS (mg/1)	VSS (mg/1)
10/2	21			8.0	8	806				48			
10/3	21			8.7	10	1149				51			
10/4	21	1420	1112	8.2	8	1137	632			56	6		
10/5	21			8.0	8	958				51			
10/6	21	1244	972	8.2	10	622				47			
10/9	18	1056	1788	7.6	13					82			
10/10	18	1108	892	7.0	25	7209				364			
10/11	19	1304	1100	7.0	23	6612				850			
10/12	19			7.0	24					689			
10/13	21			7.0	23	6481				822			
10/16	18	1448	1236	6.4	20	6467				317			
10/17	19			6.0	22	6218				826			
10/18	19	1280	1104	6.8	20	6090				749			
10/19	19	1244	1052	7.0	16	6012	3120			851	376		
10/20						5967				854			
10/24	19	1368	1208	7.0	31	5640				640			
10/25		1000	980										
10/26						5158				809			
10/27						4840				539			

(*) Coke oven activated sludge only

TABLE 13

CONTINUOUS BIOSYSTEM TREATABILITY DATA

UNIT B

Date	Mixed Liquor (*)					Influent				Effluent			
	Temp	SS	VSS	DO	DO UPT	COD	BOD_5	SS	VSS	COD	BOD_5	SS	VSS
(1978)	(^oC)	(mg/1)	(mg/1)	(mg/1)	(mg/1/hr)	(mg/1)	(mg/1)	(mg/1)	(mg/1)	(mg/1)	(mg/1)	(mg/1)	(mg/1)
8/8		180	180					11		119.2		16	16
8/9		2310	2200	7.4	18	490		4		682		977	915
8/10		2450	2240	5.2	46	375		4		509		126	114
8/11		3272	3272	5.2		307		28		596		204	
8/14		2460	1880	4.6		82	30	23		383	166	188	
8/15		2428	2380	4.6	46	442		22		279		144	
8/16		2072	1980	5.0	38	130		254		140		106	
8/17		1808	1796	5.5	30	770		19		150		58	
8/18		1844	1780	5.6	27	575		59		282		40	
8/21		1896	1840	6.4	16								
8/22													
8/23		2616	2492	5.4		890		16		276		78	
8/24		2584	2460	2.2		822		40		413		136	
8/25				3.0		750	442			382	45	104	
8/28		2288	2220	6.2	18			118		494		74	
8/29		3196	3068	7.0	12	1251		34		546		246	
8/30		2708	2564	5.4	40	1138				469			
8/31						1087				48			

(*) Coke oven activated sludge plus dry bacterial culture

TABLE 13 (Con't)

CONTINUOUS BIOSYSTEM TREATABILITY DATA

UNIT B

Date	Mixed Liquor (*)					Influent				Effluent			
(1978)	Temp (°C)	SS (mg/l)	VSS (mg/l)	DO (mg/l)	DO UPT (mg/l/hr)	COD (mg/l)	BOD_5 (mg/l)	SS (mg/l)	VSS (mg/l)	COD (mg/l)	BOD_5 (mg/l)	SS (mg/l)	VSS (mg/l)
9/5						834							
9/6		1916	1860	6.0	31	831							
9/7		2014	1908	6.4	27	913				276			
9/8	18	2098	2002	9.1	3	716	306			243	17.4		
9/11	22	2036	1884	7.6	27	641	294	30	14	230	12.6	86	82
9/12	25	2084	1898	7.6	6		246				11.4		
9/13	21	2128	1912	8.2	18	439	206			147	1.8		
9/14							176				6		
9/15	22	2156	1968	7.7	16	519	104	56	46	151	3	56	48
9/18	27	1756	1544	7.0	15	748		18	12	53		90	74
9/19	22	1308	912	8.2	9.6	901				84			
9/20	22	1320	1136	8.0	8.0	1201		60	36	80		66	30
9/21	25			7.2	22	1031				72			
9/22	26	1312	1148	7.0	27	1005				80			
9/25		1392	1208			913				60			
9/26						854				68			

(*) Coke oven activated sludge plus dry bacterial culture

TABLE 13 (Con't)

CONTINUOUS BIOSYSTEM TREATABILITY DATA

UNIT B

	Mixed Liquor (*)					Influent				Effluent			
Date (1978)	Temp (°C)	SS (mg/1)	VSS (mg/1)	DO (mg/1)	DO UPT (mg/1/hr)	COD (mg/1)	BOD_5 (mg/1)	SS (mg/1)	VSS (mg/1)	COD (mg/1)	BOD_5 (mg/1)	SS (mg/1)	VSS (mg/1)
10/2	22			7.8	14	806				52			
10/3	21			8.0	12	1149				51			
10/4	21	2040	1832	7.8	13	1137	632			48			
10/5	22			7.8	12	958				43	6		
10/6	21	2060	1780	8.0	18	622				51			
10/9	19	1340	2096	7.4	17					78			
10/10	19	2300	2040	6.8	38	7204				256			
10/11	20	1964	1764	6.8	39	6612				488			
10/12	20			6.8	39	6507				313			
10/13	21			6.4	49	6481				284			
10/16	18	2056	1876	7.6	34	6467				127			
10/17	19			7.4	34	6218				362			
10/18	19	1968	1796	7.4	32	6090				327			
10/19	19	2120	1908	7.2	38	6012	3120			343	420		
10/20						5967				338			
10/24	19	2204	2020	7.2	39	5640				448			
10/25		2024	1864										
10/26						5158				682			
10/27						4840				523			

(*) Coke oven activated sludge plus dry bacterial culture

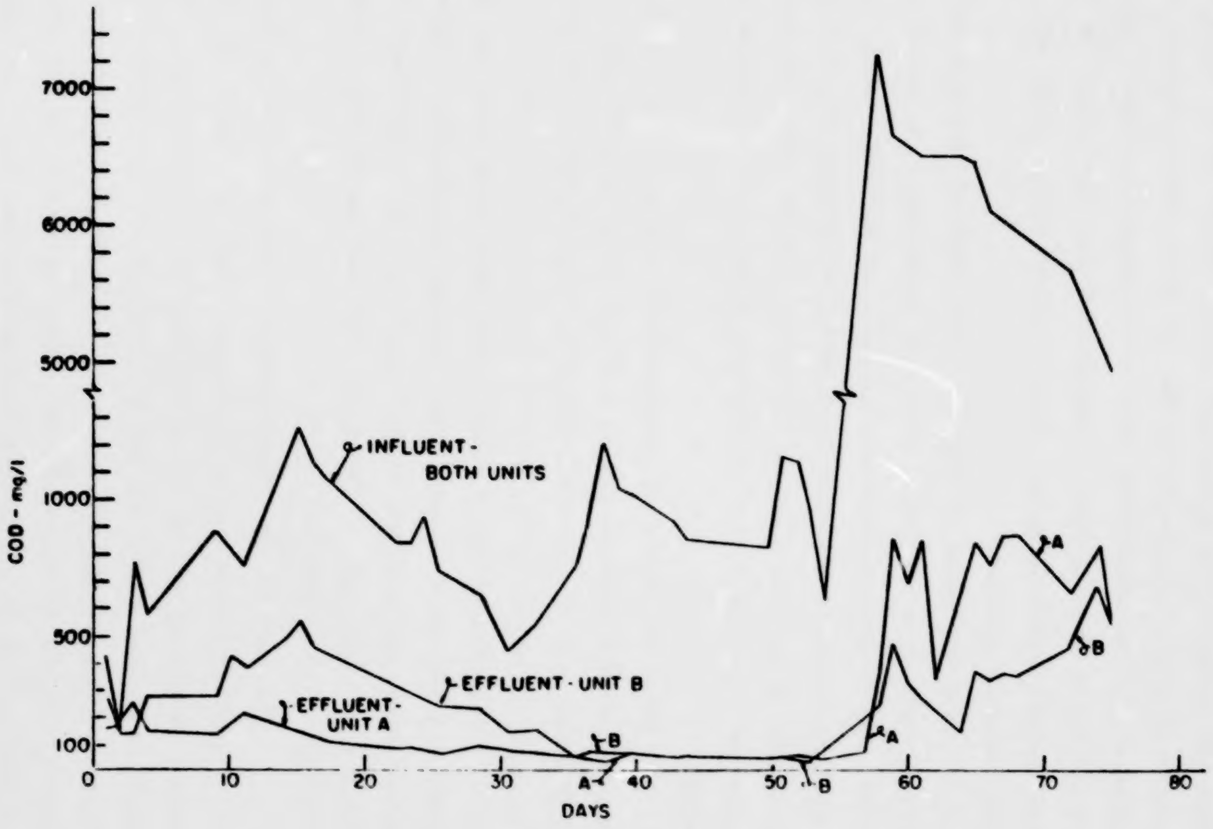


Figure 16. Continuous biological reactor results.

6.4.4 Discussion of Results

It was anticipated at the outset that the bio-oxidation (activated sludge) CA screening procedure would be fraught with many difficulties primarily related (1) to the tight time frame of about one week initially set as being reasonable for wastewater CAD, and (2) to the source of the biomass needed to conduct the treatability screening tests. Generally speaking, acclimation of a biomass to a specific waste stream requires several weeks. If the CAD time schedule was to be maintained, the CA screening procedure would have to be accomplished in several days. Substantial work was conducted during verification testing which addressed these circumstances. Both wet and dry seed approaches were studied.

Data collected during the early exploratory work with the dry bacterial culture contained a number of anomalies. It was found (1) that effluent COD concentrations were higher than effluent value, and (2) that the COD concentration in the open feed container dropped rapidly on standing. (The latter effect was very substanially reduced - but not totally eliminated - by covering the feed vessel during the subsequent continuous biotesting studies.)

Table 10 shows that the organic foods/nutrients contained in the dry bacterial culture mixture add an average of 91 mg/l BOD and an average of 205 mg/l COD per gram of culture. The COD value continues to increase with time up to 72 hours of aeration.

The phenomenon of organic (BOD/COD) loss from the synthetic waste mixture was addressed several times during verification testing through studies involving aeration of different batches of synthetic waste under varying test conditions. The data collected during these runs are presented in Tables 9A, 9B, and 11.

The bulk of the results support the proposition that the losses occur primarily through volatilization. However, there is some evidence that chemical oxidation of the organics could also be involved. Whatever the actual mechanisms might be, Table 9B and 11 (Unit #1) show that the cumulative effect of air stripping/oxidation is essentially reached after 48 hours of aeration. Table **9B** evaluates the effect of volume on BOD/COD reduction. A stripping action is definitely indicated by the fact that the (smaller) units with greater air to liquid ratios demonstrated higher reductions.

Batch testing (Table 11) revealed no significant differences in BOD and COD removals between the dry bacteria system (Unit #4) and the air stripping system (Unit #1).

Both of the systems (Units #2 and #3) using coke oven activated sludge as the bulk of the seed performed similarly, with better removals than the stripping unit and the dry bacteria unit. In these batch tests, no significant difference was observed between coke oven sludge alone (Unit #2) and the system containing supplemental dry bacterial culture (Unit #3).

Average COD and BOD removals were calculated to compare the effectiveness of the different units. After 24 hours, there was little difference among any of the reactors in either BOD or COD removal, except for Unit #1 which was somewhat lower. The units containing coke oven sludge (with and without dry bacteria) began to show greater removals at 48 hours and this trend continued for the 72 hour samples. The reactor containing dry bacteria alone showed very little, if any, superiority over the air stripping/oxidation reactor during the first day, and by the end of the test, the removals were essentially equivalent. Unit #3 (coke oven sludge plus dry bacteria) had a slightly higher COD removal rate than Unit #4 (coke oven sludge only), but the difference was so small that it cannot be attributed to the dry bacteria. BOD removals for these two units were identical.

Figure 16 shows influent and effluent COD data for both continuous units during the entire test period. During the early part of the run, the unit with dry bacteria addition (Unit B) showed higher effluent values. Vendor instructions on the use of the dry bacterial culture as a supplemental addition were followed in Unit B. The procedure specified a relatively high initial dose followed by a decreasing dosage rate until a point where only a maintenance dose is applied daily. Presumably, the effluent COD pattern demonstrated by Unit B reflects the changing dosage rate of the bacterial culture. (The effect of culture dose on effluent COD has already been discussed). When the dry bacteria addition reached the maintenance dosage level, COD removals for this system (Unit B) reached a level equivalent to the coke oven sludge system (Unit A).

During the final three weeks of testing, both units were fed full strength waste. The unit with the dry bacteria showed a much greater ability to cope with the shock loading conditions encountered when the feed was abruptly changed to full strength. The companion unit was adversely affected by the change in feed, although it gradually recovered over a three week period when, because of time limitations, operation of all units was discontinued.

Results from verification testing of the bio-oxidation CA screening procedure have produced much valuable information impacting on CAD wastewater methodolgy. If the synthetic waste mixture used in the experimental work closely simulates a real life coal conversion aqueous waste, then a substantial portion of the organic removals usually attributed to oxidation by biological organisms may well be physically stripped from the bio-reactor as an air emission. Consequently, a simple aeration step in parallel with the biological treatment step appears warranted to ascertain the extent to which organic removals through stripping/oxidation is occurring.

Based on results developed with one commercial dry bacterial culture mixture, the use of this type of dehydrated product as a biological seed does not meet the needs of the CA screening procedure. A wet seed approach must be adopted. Moreover, the wet seed must be acclimated for about 3 weeks to a waste stream which is generally descriptive of the material that will eventually be tested by the CA procedure.

Clearly, two choices present themselves. One is to disregard the biological oxidation step entirely, which is not really reasonable, since this approach will eliminate consideration of the effects of a major waste treatment unit process. The second option is to begin biological acclimation (using a locally available activated sludge as seed) three weeks in advance of the CA wastewater screening study. During this time, the CA team could be generating the air samples for IERL Level 1 analyses.

At the outset of verification biotesting, it was presumed that the CA team would use COD analyses as the prime performance monitoring method, backed up by an occasional reference BOD. In view of the experiences gained during this test work, some doubt is now cast upon the validity of using COD for these purposes. Changes produced by aeration in the oxidation state of dissolved waste organics may be clouding the dichromate chemistry with the possibility of producing misleading data. It would appear that the CA team should be equipped with a TOC analyzer for quantifying waste organic content and for process monitoring purposes.

6.5 ION EXCHANGE

6.5.1 Initial Concepts

Ion exchange resins are used to extract inorganic cations and anions from liquids. It is expected that coal conversion wastewaters will contain a large variety of impurities which have the potential for being removed by some type of exchange resin. Ion exchange resins are made to selectively remove certain ions from solution, and therefore, a single resin cannot be expected to achieve high removals over the broad range of ions possible in the wastewater. The driving force mechanisms encountered with ion exchange resin operation are analogous to those for activated carbon, and for this reason, batch treatment by resins is much less effective than a continuous flow column system. A series of columns each containing a specific resin would be the optimal configuration for removal of the largest amount of impurities.

6.5.2 Selected Alternative

After discussions with an ion exchange resins manufacturer, it was decided to employ a three (2-inch I.D.) glass column system set up in series. The first column contained a strong-acid type resin, while the second column was filled with a weak-acid resin. The final column contained a strong-base resin. Prior experience by the manufacturer suggested that this combination of resins would remove the majority of ions expected to be present in a typical coal conversion wastewater. To minimize pumping requirements, a single pump was to be used to introduce the sample into the first column, and by proper positioning of the second and third columns, a continuous gravity flow would be maintained.

6.5.3 Test Work

The ion exchange system was tested to evaluate its ability to process the required aqueous sample within one work day. Excess solids in the wastewater caused a flow rate problem in the columns which was solved by filtering the sample through the 75-micron cartridge and changing the resin bed support media. A single pump was used to introduce the wastewater into the first column, and gravity flow was employed through the second and third columns. Constant adjustments to the column height and piping were necessary to produce a continuous flow through all of the columns.

CAD methodology specifies the use of ion exchange at two points in the test sequence (Figure 13; after bio-oxidation; and after bio-oxidation plus carbon adsorption. Reference analyses of a few selected metals were made for these runs and the results are shown on Table 14.

6.5.4 Discussion of Results

The gravity flow concept is not acceptable since unequal pressure drops through the columns, caused primarily by differences in resin particle diameters, necessitated constant adjustments to the column heights to maintain a continuous flow. It has been determined that the sample should be pumped through one column at a time to eliminate this problem. Furthermore, to reduce the possibility of plugging the resins with solids, a cartridge filter should be placed in line before the first resin column.

The analytical data indicate that the ion exchange resins did remove metals, although there was some performance variability from metal to metal. The principal impact on CAD methodology is that an overall comparison of the effluents from both runs show them to be reasonably similar. Therefore, these results suggest that two ion exchange runs are not required for CAD purposes. The ion exchange run after carbon adsorption is the more appropriate site selection in the test sequence.

In view of the increase in column size (from 2-inch to 3-inch I.D.) suggested for the carbon CA screening procedure, it is logical to also change the ion exchange column size to 3 inches. This alteration will gain some time during the ion exchange test run and will serve to standardize the column sizes for both screening procedures.

TABLE 14

RESULTS OF ION EXCHANGE TESTING

Parameter	Influent	Run #1 Effluent	Run #2 Effluent
Iron as Fe, mg/l	0.7	1.5*	0.7
Copper as Cu, mg/l	0.18	N.D.	0.034
Cadmium as Cd, mg/l	0.06	0.05	0.05
Zinc as Zn, mg/l	0.36	0.22	0.15

Notes

Run #1 was made on a sample after bio-oxidation plus carbon adsorption.

Run #2 was made on a sample after bio-oxidation only.

N.D. Indicates Not Detectable (less than 0.05 mmg/l).

*Possible contamination from equipment fittings.

SECTION 7

CONCLUSIONS AND RECOMMENDATIONS - WASTEWATER

Laboratory verification of the CAD screening procedures revealed several problems with the original wastewater methodologies. Minor equipment changes were made to facilitate sample handling and a revision of the biological oxidation procedure was necessary. Figure 17 shows the steps in the initial CAD treatment sequence and includes verification testing results for those processes examined.

Conclusions and recommendations developed from the study are:

- Solids separation using an in-line cartridge filter presented no difficulty and this approach will be adopted as originally conceived.

  Supplemental solids filtrations may be required, if precipitates form in the wastewater sample, to prevent blinding of the carbon and/or ion exchange resin beds.
- Carbon adsorption should remain where proposed by the CAD wastewater methodology, i.e., both before and after bio-oxidation.
- The carbon column diameter should be changed from the 2-inch I.D. specified to 3 inches. A few minor column design modifications are also suggested.
- Verification testing data strongly support the proposition that a substantial portion of the BOD and COD removals demonstrated during the bio-oxidation screening procedure can be attributed to air stripping (volatilization). Therefore, the CAD wastewater methodology should be modified to include an air stripping step running in parallel with the specified bio-oxidation screening procedure.

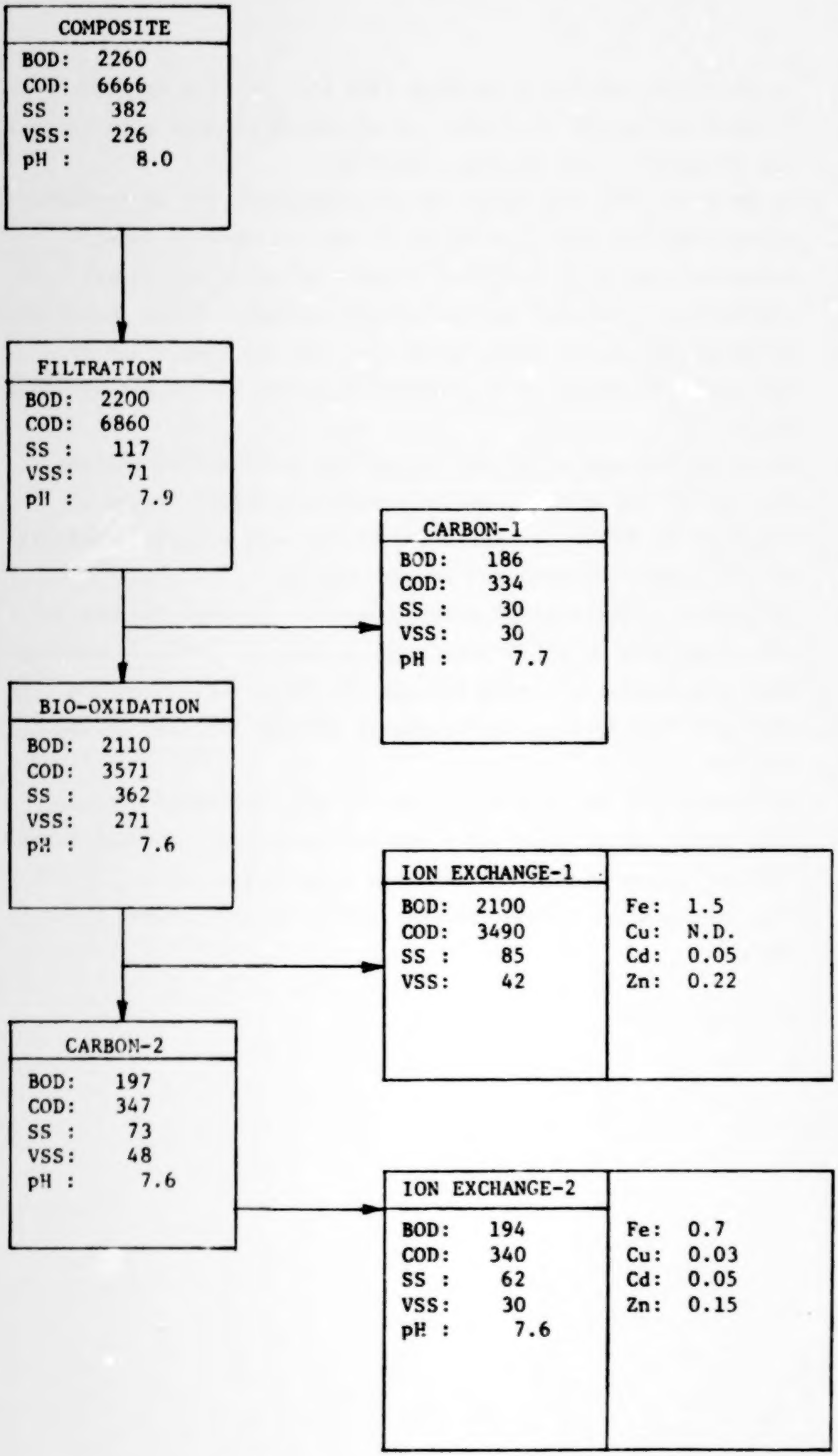

COMPOSITE
BOD: 2260
COD: 6666
SS : 382
VSS: 226
pH : 8.0
FILTRATION
BOD: 2200
COD: 6860
SS : 117
VSS: 71
pH : 7.9
CARBON-1
BOD: 186
COD: 334
SS : 30
VSS: 30
pH : 7.7
BIO-OXIDATION
BOD: 2110
COD: 3571
SS : 362
VSS: 271
pH : 7.6
ION EXCHANGE-1
BOD: 2100
COD: 3490
SS : 85
VSS: 42
Fe: 1.5
Cu: N.D.
Cd: 0.05
Zn: 0.22
CARBON-2
BOD: 197
COD: 347
SS : 73
VSS: 48
pH : 7.6
ION EXCHANGE-2
BOD: 194
COD: 340
SS : 62
VSS: 30
pH : 7.6
Fe: 0.7
Cu: 0.03
Cd: 0.05
Zn: 0.15

Figure 17. Results for synthetic waste sample.

- Insufficient benefit is derived from the use of a dry bacterial culture during the bio-oxidation screening procedure to warrant its adoption in the testing procedure.
- To be effective, bio-oxidation screening must use an activated sludge that has been acclimated to the wastewaters under consideration for a period of 3 weeks prior to the formal initiation of the CAD wastewater methodology. While acclimation is under way, it is anticipated that the CAD team would be pursuing the screening procedures specified by CAD air methodologies.
- Based on experience derived during the verification testing, the use of COD analyses as the monitoring method should be replaced by TOC to provide a faster and more accurate analysis of the organic composition of the samples.
- The gravity flow concept through the ion exchange columns is not acceptable as a CAD screening procedure. It is recommended that the sample be pumped through the first column and the effluent from each column be pumped through the next column in series.
- Evaluation of the effects of ion exchange should be studied only after carbon adsorption and not before it. The wastewater testing sequence should be altered accordingly.
- The ion exchange column diameter should be standarized at 3 inches.

SECTION 8

GASEOUS EMISSIONS SCREENING

8.1 GAS BLEND COMPOSITION

A special gas blend was utilized during verification testing which had the following composition:

Carbon Dioxide	-	70%
Nitrogen	-	29.55%
Hydrogen Sulfide	-	2000 ppmv
Ethylene	-	2500 ppmv

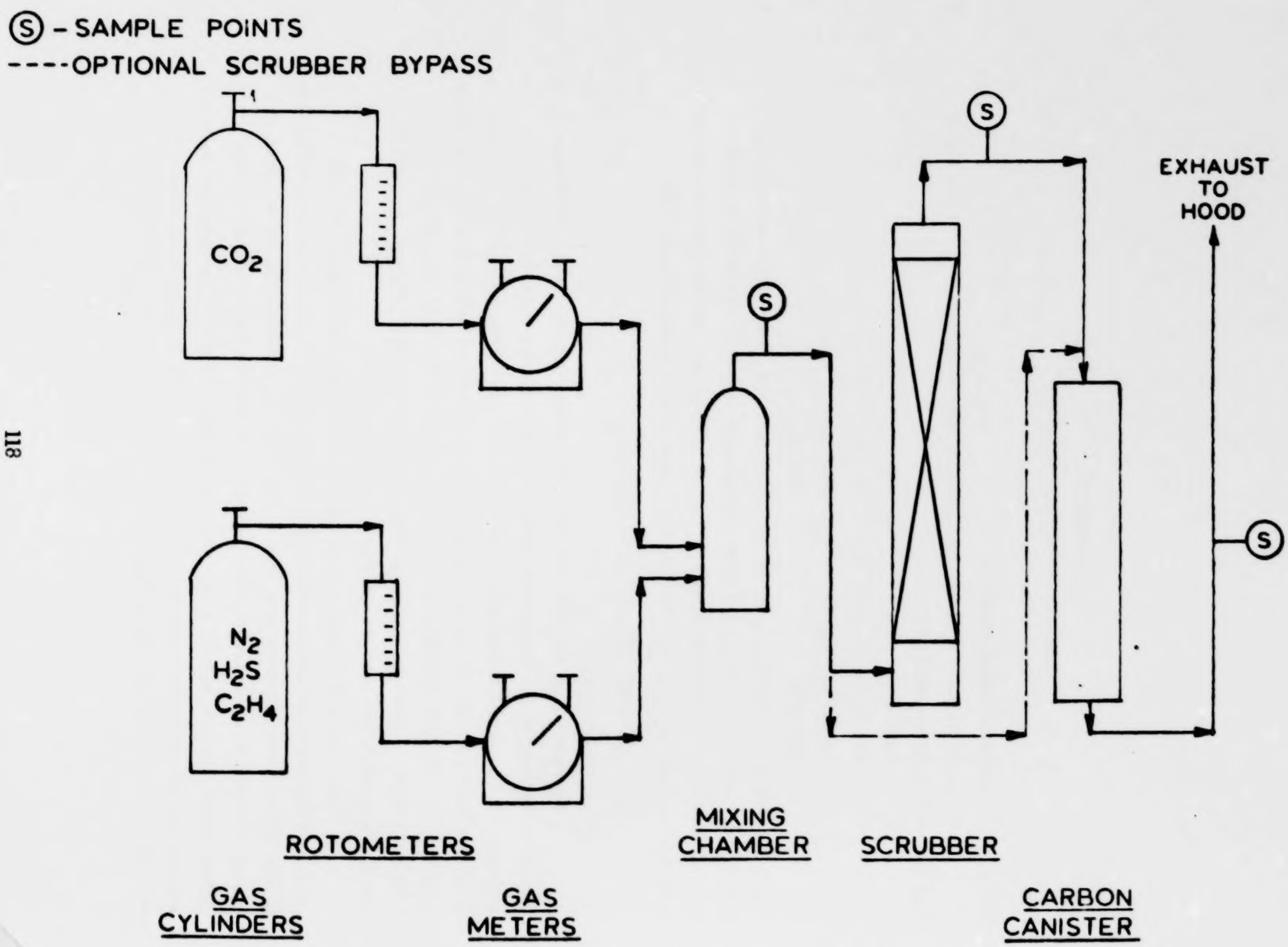
Two gas cylinders were required to obtain this blend, the first containing the N_2, H_2S and C_2H_4, and the second containing the CO_2. Flow rates from both cylinders were monitored by the use of rotameters and dry gas meters and were adjusted to obtain the desired final gas composition (Figure 18).

8.2 MODIFIED SAMPLING SYSTEM EVALUATION

8.2.1 Initial Concepts

In developing the CAD air methodologies, typical unit operations needed to remove particulates and gases/vapors from air emissions were evaluated. For various reasons, some of these operations had to be excluded from consideration as CA screening procedures. Control technologies eventually selected for the CAD methodology included; particulate removal, gas cooling (condensation), carbon adsorption, and liquid scrubbing. Figure 19 presents the gaseous emission testing sequence.

The Source Assesment Sampling System (SASS) developed for IERL Level 1 sampling made use of all these mechanisms for separation and collection of gas stream contaminants, and therefore, initially seemed to be an ideal system for use in CA screening procedures. It was thought that activated carbon could replace XAD-2 in the same cartridge. However, subsequent calculations showed that the capacity of the standard XAD sorbent module used in the SASS train would not be adequate for CA studies.



Ⓢ - SAMPLE POINTS
----OPTIONAL SCRUBBER BYPASS
CO_2
N_2
H_2S
C_2H_4
Ⓢ
Ⓢ
Ⓢ
EXHAUST TO HOOD
ROTOMETERS
MIXING CHAMBER
SCRUBBER
GAS CYLINDERS
GAS METERS
CARBON CANISTER

Figure 18. Scrubber evaluation apparatus.

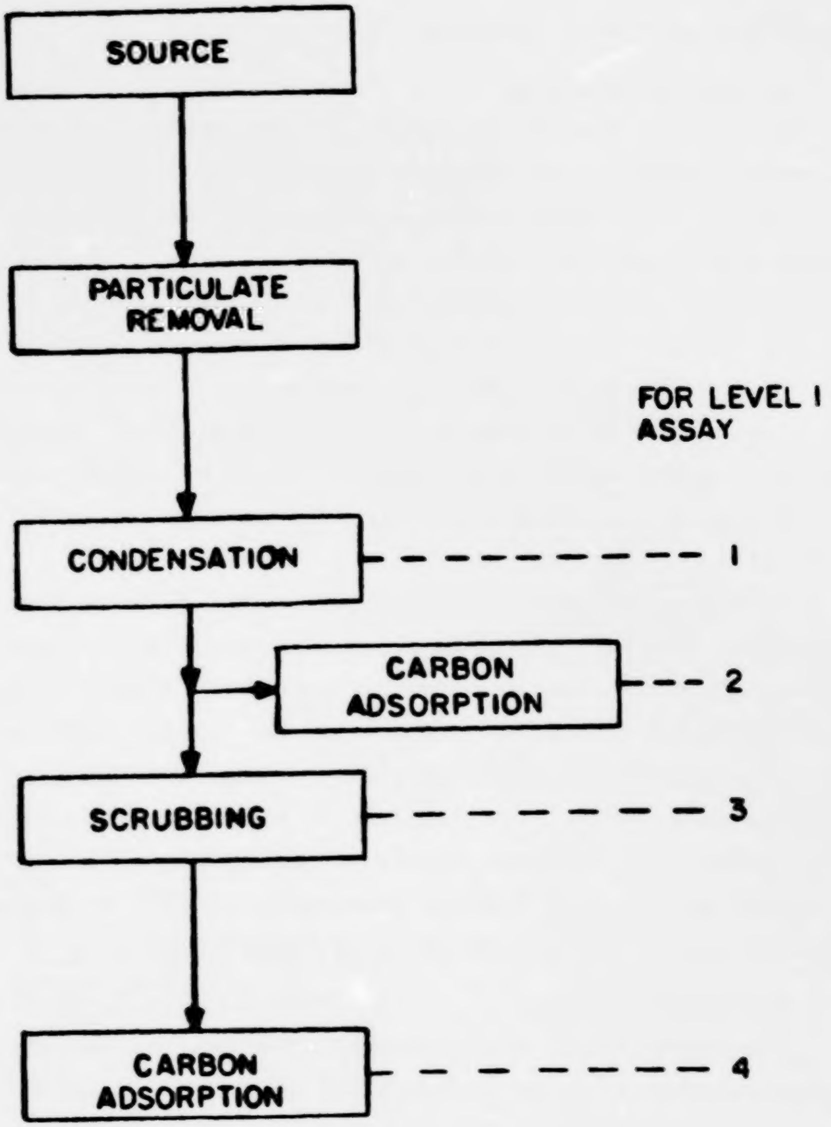

SOURCE
PARTICULATE REMOVAL
FOR LEVEL I ASSAY
CONDENSATION
1
CARBON ADSORPTION
2
SCRUBBING
3
CARBON ADSORPTION
4

Figure 19. Gaseous emission test sequence.

Several scrubbing media were investigated and sodium carbonate was selected as the most promising. The capacity needed to remove acidic components at expected concentrations was also calculated, and it was determined that the standard SASS impinger assembly would not hold the required volume. The existing condensation module in the SASS train was not expected to be a problem, since sample flow rates and test duration would be similar to those encountered in IERL Level 1 sampling.

8.2.2 Selected Alternative

In order to provide the extra capacity required for scrubbing, a counter-current packed column scrubber with an 8-liter reservoir was designed. A 4-inch I.D. by 5-foot glass column containing 3 feet of Raschig rings as packing was used during verification testing.

Likewise, a larger canister to contain the activated carbon was designed. A 4-inch I.D. by 3-foot glass column containing 10 lbs. of activated carbon (3-foot bed depth) was used for testing.

Figure 20 shows the configuration of the modified screening train as assembled to evaluate scrubbing followed by activated carbon. Both control technologies can be evaluated separately, if a process review indicates no need to study both systems in series.

The solids removal module of the standard SASS has been incorporated into the train. However, particulate removal technology will not be evaluated during CA screening, because data for evaluating the effects of solids removal technologies/control devices are obtained by the standard IERL Level 1 sampling procedures, as amended by CAD methodologies. When sampling a gas stream with a high particulate loading, this module will prevent particle build-up on the activated carbon. The condenser module serves two purposes: for cooling of the gas stream (to a carbon influent temperature of 55°C or less); and as a separate unit process for removal of low-boiling organics.

8.2.3 Test Work

The standard SASS train presently requires two vane-type pumps arranged in parallel in order to maintain a sample flow rate of 4 cubic feet per minute through the sample collection portion of the train.

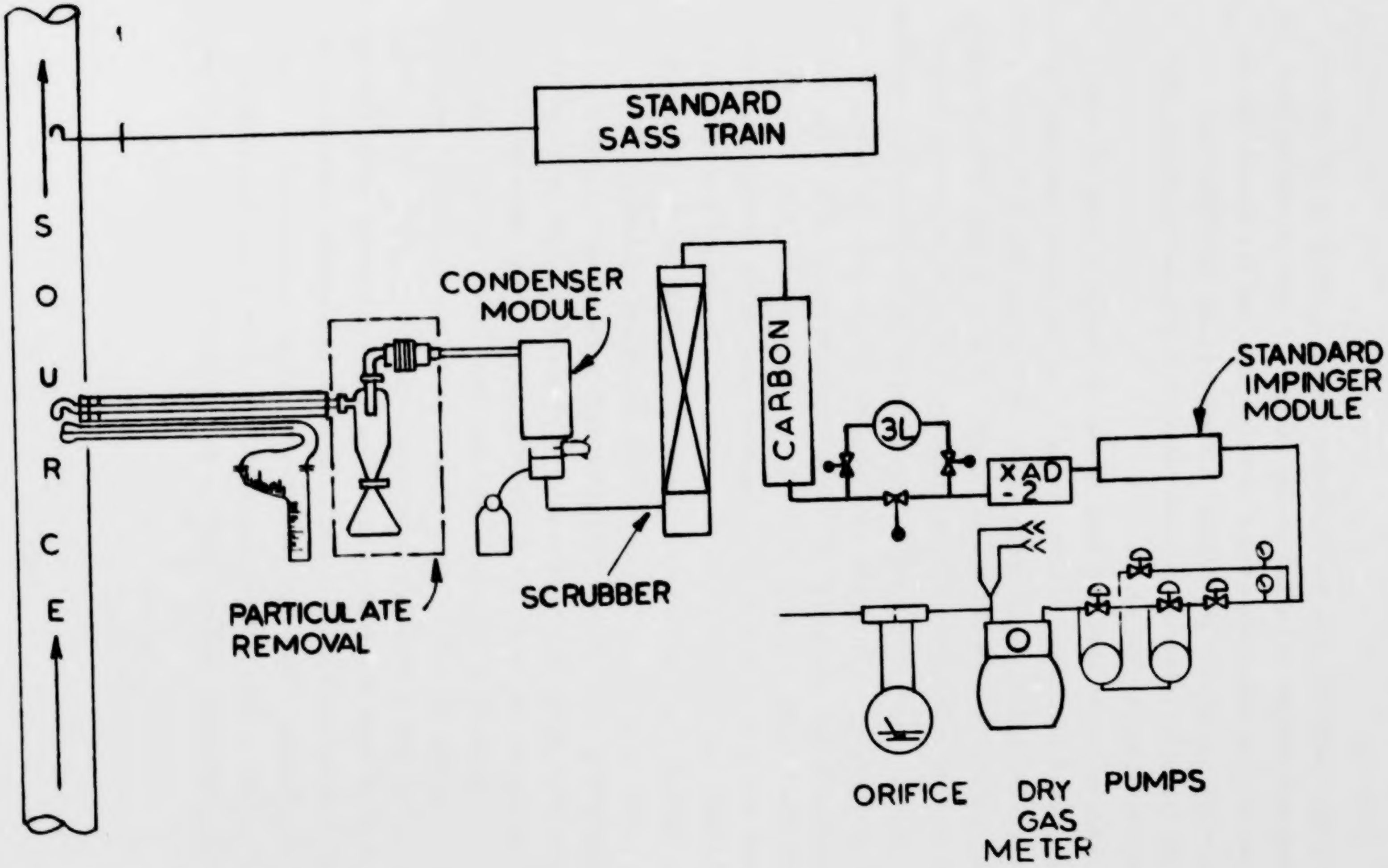

STANDARD
SASS TRAIN
S
O
U
R
C
E
CONDENSER
MODULE
PARTICULATE
REMOVAL
SCRUBBER
CARBON
3L
XAD
-2
STANDARD
IMPINGER
MODULE
ORIFICE
DRY
GAS
METER
PUMPS

Figure 20. Combination scrubbing and carbon adsorption screening train.

During a sampling run, particulates gradually build up on the filter causing an increase in vacuum at the pumps. If this vacuum becomes too great, the desired flow rate cannot be maintained and the system must be shut down in order to replace the filter. Incorporating two additional modules in the train (scrubber and carbon adsorption modules) increases the total pressure drop across the system.

A SASS train was obtained from the manufacturer to quantify the effects of the added components on the system. Testing was accomplished by drawing room air through the SASS train alone, SASS train with carbon in-line, and the complete system (SASS plus carbon canister and scrubber modules). Vacuum hoses with an I.D. of one-quarter inch were used to connect the extra modules to the SASS train. Tests were also performed to determine the pressure drop across these lines. All vacuum readings were taken from the gauges supplied with the pumps, and gas flow rate measurements were made using the gas meter and timer which are part of the SASS train control unit. Before the tests were conducted, a filter was placed in the filter holder, three of the impingers were each filled with 750 milliters of tap water and the fourth impinger was charged with silica gel. XAD-2 resin was placed in the sorbent cartridge assembly. Results of these tests are presented in Table 15.

Preliminary calculations indicated that 8 liters of scrubbing solution (1-Normal sodium carbonate) would be required to scrub 1000 ft^3 of sample with an H_2S concentration of approximately 2000 ppmv. Additional calculations indicated that five pounds of activated carbon would be adequate for removal of organic compounds expected in a waste gas stream. To verify these calculations, the special gas blend was used.

The gases were first introduced into a mixing chamber where initial samples were taken to determine both H_2S and total hydrocarbon concentrations. From the mixing chamber, the gases then flowed through the scrubber unit and the carbon canister. Several test runs were made on each unit separately, and one run was conducted to determine H_2S and hydrocarbon removals with both

TABLE 15

SCREENING TRAIN PRESSURE DROP TESTING

	Flow Rate (cfm)	Vacuum (in. Hg)	Flow Rate (cfm)	Vacuum (in. Hg)
Standard SASS	4.0	8.5	3.0	6.0
Scrubber and Connecting Lines	4.0	8.5	3.0	5.0
Connecting Lines (Only)	4.0	6.5	3.0	4.0
Scrubber	4.0	2.0	3.0	1.0
Carbon Columns and Connecting Lines	4.0	5.0	3.0	4.0
Connecting Lines (Only)	4.0	4.5	3.0	3.5
Carbon Columns	4.0	0.5	3.0	0.5
TOTAL SYSTEM	4.0	18.5	3.0	9.0
(Standard SASS with both scrubber and carbon columns on-line)			3.7	15.0

units in series. Total hydrocarbons were measured by taking a 100 ml gas sample and injecting directly into a gas chromatograph equipped with a flame ionization detector. Methane was used as the standarization gas, and therefore, the results are presented as total hydrocarbons expressed as methane. Hydrogen sulfide levels were measured by drawing a sample of the gas directly through H_2S detector tubes. Results of the testing are presented in Tables 16-19.

8.2.4 Discussion of Results

The particulate collection system used in the standard SASS train consist of 3 cyclone separators in series followed by a fiberglass filter. The cyclones have nominal cut-points of 10μ, 3μ and 1μ, respectively. The fiberglass filter is used to collect particles smaller than 1μ. Proper operation of the cyclones is dependent on the sample gas flow rate through the system, with 4 cfm being the optimum design flow rate. At this rate, a typical test run collecting 1000 cubic feet of sample has an approximate duration of 4.5 hours. Depending on particulate loading in the gas stream, it may become impossible to maintain a 4 cfm flow rate through the modified SASS train (scrubber and carbon modules in line); however, the only problem this presents is an extended sampling period. For the purposes of the CA screening procedures, it is not absolutely necessary to maintain the 4 cfm flow rate.

The laboratory testing was performed using 1/4-inch I.D., heavy-wall vacuum tubing for connection of the screening modules to the SASS train. The sample flow piping in the standard train is 1/2-inch I.D., and it is recommended that this size tubing be used for the design of the actual screening train to eliminate the pressure drop caused by the smaller diameter tubing. The modular construction of the entire screening train makes it a simple matter to add or delete components or rearrange the sequence of any of the units, depending on prior knowledge of the gas stream constituents and/or the desired application of the train at a particular source.

From SASS train work experiences reported by others, it is estimated that three men will be able to perform a complete screening test on a single source in a time period of two days. Considering the possibility of encountering multiple sources in a plant, it becomes obvious why a plan of selective sampling based on process knowledge is of paramount importance in this program, if total field time is to be controlled within acceptable limits.

TABLE 16

Run #1 - SCRUBBER EVALUATION

Time (minutes)	Gas Volume (cubic feet)	Inlet Concentration		Outlet Concentration		% Removal	
		H_2S (ppm)	Total Hydrocarbon*	H_2S (ppm)	Total Hydrocarbon*	H_2S	Total Hydrocarbon
0	0	1800	1301	4	1770	99.7	-
30	29.2	1960	-	3	-	99.8	-
60	78.5	2000	1344	3	2560	99.8	-
90	116.3	2000	-	100	-	95.0	-
95	124.9	1800	939	200	1088	88.9	-
100	131.3	1150	-	360	-	68.6	-
115	144.7	1900	683	600	704	68.4	-
130	166.8	2000	-	900	-	55.0	-
145	195.0	2000	-	1150	-	42.5	-

* ppm as methane

TABLE 17

RUN #2 - SCRUBBER EVALUATION

Time (minutes)	Gas Volume (cubic feet)	Inlet Concentration H_2S (ppm)	Outlet Concentration H_2S (ppm)	% Removal H_2S
0	-	2800	10	99.6
10	11.4	2400	50	97.9
20	21.5	2200	45	97.9
35	39.4	2200	100	95.4
50	55.6	2200	210	90.4
65	73.1	2400	400	81.8
80	93.1	2200	810	63.1

TABLE 18

RUN #1 CARBON ADSORPTION

Time (minutes)	Gas Volume (cubic feet)	Inlet Concentration		Outlet Concentration		% Removal	
		H_2S (ppm)	Total Hydrocarbon*	H_2S (ppm)	Total Hydrocarbon*	H_2S	Total Hydrocarbon
0	-	2100	1148	2	901	99.9	21.5
15	26.5	2100	1193	2	1190	99.9	-
25	53.3	2400	-	200	-	91.6	-
40	63.8	2400	1418	500	1418	79.1	-
45	71.1	2350	-	1000	-	57.4	-

* ppm as methane

TABLE 19

RUN #1 - SCRUBBING FOLLOWED BY CARBON ADSORPTION

Time (minutes)	Gas Volume (cubic feet)	Inlet Concentration		Outlet Concentration		% Removal	
		H_2S (ppm)	Total Hydrocarbon*	H_2S (ppm)	Total Hydrocarbon*	H_2S	Total Hydrocarbon
0	-	2400	1060	5	1000	99.8	5.7
25	37.2	2400	1250	10	1275	99.6	-
60	94.6	2100	-	40	-	98.1	-
90	143.2	2200	-	100	-	95.4	-
105	167.1	2400	-	240	-	90.0	-
120	192.6	2200	-	500	-	77.2	-
150	240.6	2400	-	1250	-	47.9	-

* (ppm as methane)

The results of pilot scrubber testing (see Tables 16 and 17) indicate that 8 liters of sodium carbonate scrubbing solution will not be adequate when drawing a 1000 cubic foot sample which has an acid gas concentration (H_2S, SO_2 etc.) of 2000 ppmv or greater. It was observed during the test period that the scrubber solution became totally ineffective at a pH of 10.0 or less. It is recommended that the solution concentration be increased to 2-Normal, and that the total volume available in the reservoir be increased to 16 liters. As an extra precaution, a pH meter should be used to monitor the condition of the scrubbing medium. If it is necessary to halt the run for a filter change at any time during the test, the scrubbing solution should also be replaced at that time.

Removal of ethylene from the test gas stream by activated carbon was very poor (Tables 18 and 19). It is not known whether this was due to an inherently low adsorption capacity for this compound onto the test carbon, or if the large quantity of carbon dioxide present in the stream resulted in flushing the ethylene through the system. Organics with higher molecular weights stand a much better chance of being adsorbed on the carbon, and for this reason, it is recommended that the carbon module be retained in the screening program. It is not practical to substantially increase the amount of carbon used in the screening train because (1) the train already consists of many modules which are large enough to present problems when the sample location is difficult to reach, and (2) space at the sample point will be restricted in most cases. The CA screening procedure for carbon during Level 1 may be somewhat limited, but will nevertheless be indicative of the potential of the process for removing organic contaminants, and serve as a guide for future studies.

In order to obtain meaningful results from the CA tests, it is imperative that each source to be evaluated be sampled according to the Level 1 IERL methods in addition to the screening sampling. Ideally, both tests will be run simultaneously. If this is not possible, process data for each source must be evaluated to determine the constancy of operation and judgement must be used to assess the reliability of comparing data from two non-simultaneous test runs.

SECTION 9

CONCLUSIONS AND RECOMMENDATIONS - GASEOUS EMISSIONS

Laboratory verification tests indicated that the use of a SASS train is feasible for CA screening procedures when the following modifications have been made:

- The organic adsorbent module and impingers indigenous to the SASS equipment train are not of suitable size for use in CA screening procedures. The screening procedures using scrubbing and carbon adsorption specified by CAD air methodologies should be adopted.
- Special supplemental scrubber and adsorber modules will be required for gaseous CA screening procedures to be used in conjunction with the SASS equipment. Typical supplemental modules for these unit operations were tested in the laboratory.
- For CA screening procedures, it is acceptable to reduce the sample gas flow rate to 3 cfm.
- pH of the scrubber liquid should be monitored and replaced when it falls below 10.0 standard pH units.

REFERENCES

1. Standard Methods for the Examination of Water and Wastewater. 14th Edition. 1975.

2. Hamersma, J.W., Regnolds, S.L., and Maddalone, R.F. IERL-Procedures Manual: Level 1 Environmental Assessment. EPA-600/2-76-160A. June 1976.

3. Federal Register. Standards of Performance for New Stationary Sources. Volume 36. No. 247. December 23, 1971.

4. Blake, D. Operating and Service Manual - Source Assessment Sampling System. Aerotherm Report. UM-77-80. March 1977.

5. Singer, P.C., et al., "Assessment of Coal Conversion Wastewater: Characterization and Preliminary Biotreatability," EPA 600/7/78-181, pp. 95.
6. Beychok, Milton R., "Coal Gasification and the Phenosolvan Process," presented at the 168th National Meeting of the American Chemical Society-Division of Fuel Chemistry, Atlantic City, N.J. September 1974, Volume 19 No. 5, pp. 85-93.